The role of environmental and management factors in the accumulation and plant bioavailability of cadmium in New Zealand agricultural soils

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Zicheng Yi

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Lincoln University
Te Whare Wānaka o Aoraki

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Abstract of a thesis submitted in partial fulfilment of the

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The role of environmental and management factors in the accumulation and plant bioavailability of cadmium in New Zealand agricultural soils

by

Zicheng Yi

Cadmium (Cd) accumulation in agricultural soils is a global issue, because its transfer to edible parts of common crop plants can pose a risk to food security. Soil Cd concentrations in NZ agricultural systems have been elevated due to the application of Cd-rich phosphorus fertilisers. The aim of this work was to investigate options for managing the potential Cd risk in NZ agricultural soils.

To assess the main environmental factors determining Cd uptake into plants in the NZ soil environment, more than 500 soils and paired plant (edible parts) samples from around 100 cropping sites where lettuce, spinach, onion, potato and wheat were grown were collected. The results showed that mean Cd concentrations in lettuce, wheat, onion and potato were much lower than the maximum level of Cd in the Food Standard of Australia and New Zealand (FSANZ ML) of 0.1 mg kg^{-1} (fresh weight, FW). The mean Cd concentration in baby spinach and bunching spinach was 0.08 mg kg^{-1}, with plant Cd concentrations at some sites approaching or exceeding this current NZ food standard. Around 7% of wheat grain samples also exceeded 0.1 mg kg^{-1} (FW). The effects of plant types and cultivars on plant Cd concentration were significant but varied between growing sites (regions) in this study. Multivariate regression analysis found that soil Cd concentration, pH and region could be used to estimate Cd concentrations in onions, while soil Cd concentration and carbon content could predict Cd concentration in bunching spinach. However, no significant relationships between plant Cd concentration and soil properties were observed in wheat grain and potato tuber. At a national scale, Cd concentrations in spinach and onion positively correlated with soil (pseudo) total Cd concentrations. Potato and wheat grown in Canterbury had a larger potential to accumulate Cd, although soil Cd concentrations in Canterbury were lower than in other regions.

To investigate the relationship between soil Cd bioavailability and environmental factors in more detail, 147 paired soil and plant samples were randomly selected from the national survey for a more targeted investigation. Different methods were used to test the bioavailability of the Cd (pseudo-total and porewater concentrations, 0.05 M $Ca(NO_3)_2$-extraction and diffusive gradients in thin-films, DGT). Information on a variety of soil and climatic variables were also collected. The ability of these methods to predict the Cd concentrations in the various plant samples were then compared. The bioavailability testing showed that the predictive capability of these four methods varied between plants, with no single test providing an adequate prediction for all four species. Multivariate regression analysis showed that, once certain soil and climatic variables were accounted for, $Ca(NO_3)_2$ extractions could provide a satisfactory prediction of Cd uptake by onions and spinach, while the Cd accumulation in potato tuber and wheat grain were affected by various environmental factors, including: soil variables, fertiliser status, climatic condition and plant Zn concentration. The results of the bioavailability tests indicated that various environmental factors can combine to determine the uptake of Cd by different crop species and should be considered when estimating the risks posed by Cd in agricultural soils.

Field trial experiments were conducted to evaluate the effects of lime (and sulphur) and municipal compost and their interactions on Cd uptake by potato and wheat. Three potato trials and one wheat trial were established. Cd concentrations in soil $Ca(NO_3)_2$ extractions and the edible plant parts were measured. The results showed that the application of lime and compost influenced $Ca(NO_3)_2$ extractable Cd concentration significantly in four trials. However, the changes in soil pH and organic carbon concentration by amendment addition did not achieve significant effects on Cd concentration in potato. Liming significantly increased Cd concentration in wheat grain. The variability of Cd concentrations in plant edible parts between potato and wheat across sites highlighted that the effects of lime and compost on soil Cd immobilisation were site dependent.

Finally, a modelling exercise (SCM) was used to evaluate the effects of soil types, farming practices, irrigation levels, P application rate and Cd concentration in fertiliser on soil Cd accumulation. The SCM model was validated using soil monitoring Cd concentrations at the Winchmore long-term irrigation and fertiliser trials. The estimated soil Cd concentrations from the SCM model agreed closely with the topsoil measured Cd concentrations between 1952 and 2003. The SCM simulations suggested that fertiliser Cd concentration played an important role in soil Cd enrichment. The SCM model revealed that organic soils have the largest potential to accumulate Cd. In the next 25 years, soil Cd concentration in the Waikato may experience a slight increase with over 50% of dairy farms

where soil concentrations would be likely to reach 1.0 mg Cd kg^{-1} soil, while no obvious tendency of soil Cd concentrations to increase is predicted in Canterbury, if the choice and rate of fertiliser products is allowed for when following the TFMS.

This body of work highlights the risk in using soil variables as guidelines to manage the Cd accumulation in plants under field conditions. It is concluded that Cd accumulation in plants is soil and plant factors dependent. Also, Cd concentration may continue to increase in some organic C-rich soils and soils with intensive use of P fertilizers.

Keywords: Cadmium contamination, bioavailable Cd, Trace element, Soil amendments, Heavy metals, Lime, Compost, Phosphorus fertiliser, Mass balance, Lettuce, Spinach, Onion, Potato, Wheat, Cultivar, Soil property, Diffusive gradient in thin films (DGT), $Ca(NO_3)_2$-extraction.

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Chapter 1

Introduction

1.1 Cadmium in the biosphere

Cadmium is well-known as a biologically cumulative environmental toxic contaminant (Satarug et al., 2017). When the metal that is present in soil and water is taken up by certain organisms, it can accumulate in the human body via food chains. Generally, Cd is present in all natural soils at low levels between 0.1 and 1.0 mg kg^{-1} (Nriagu, 1980). It occurs commonly in association with Zn minerals and its natural sources mainly include rock weathering, forest fires and volcanic emissions. However, intense industrialization, expanding population and accelerated urbanization in the last few decades have contributed to its rapid accumulation. Consequently, more than 90% of Cd in the worldwide surface environment is from anthropogenic sources, such as mining, waste disposal, vehicle exhausts, fertilizer use, and sewage irrigation (Loganathan et al., 2012). For example, Wei and Yang (2010) reported that almost all soil concentrations of Cd in 41 main cities from China were higher than their background values. The typically estimated half-life of Cd in soil is up to thousands of years (Alloway, 1990). As soils have a considerable capacity to retain Cd, the continuous input of Cd may keep enhancing soil Cd accumulation (Kelliher et al., 2017; Taylor, 1997). In NZ agricultural systems, the application of phosphorus (P) fertilizer is an important source of additional Cd in soil (Gray et al., 2003a; Loganathan et al., 2008). Upon being introduced into the soil environment, a certain fraction of the total Cd present can be taken up by plants. When the metal accumulates in edible parts of common crop plants, which can pose a risk to the food security of consumers (He & Singh, 1994; Jiao et al., 2012; McLaughlin & Singh, 1999). The data from the 2016 NZ total diet study indicated that *ca*. 38% of tested food samples (n=1056) had Cd concentrations higher than 0.01 mg kg^{-1} (Pearson et al., 2018). For children with age from 5 to 6 years, vegetables and grains related foods contributed to over two-thirds of their dietary Cd.

Following the introduction to topsoil, Cd will be subject to taking part in a number of chemical reactions, such as direct sorption to soil colloids, reaction with inorganic and organic ligands with possible subsequent adsorption of the metal-ligand complexes to soil colloids, precipitation as compounds with varying solubility, as well as biotic uptake by plants and other soil organisms (Loganathan et al., 2012). Being an element, the total concentration of Cd in soil can only be reduced by physically removing it or by dilution. In agricultural systems, these are often achieved by plant uptake, leaching, removing the top soil and landfilling it or by mixing the contaminated soil with less contaminated soil. It follows that, in any given soil environment, Cd can exist in a wide variety of forms, or 'chemical species'. In this thesis, 'bioavailable' Cd is considered to sum of the Cd species

that are either available, or can be made available, for uptake by the plant in question, between planting and the harvesting of its edible parts. The concentration of dissolved Cd in soil pore water is a key determinant of the extent to which the metal can be lost from soils through biological uptake or leaching (Loganathan et al., 2012; Smolders & Mertens, 2013; Soriano-Disla et al., 2010). Similar to other cations, such as Pb, Cu and Zn, it is generally thought that Cd in the form of free Cd^{2+} is passively taken up by plants (Hooda, 2010). However, there is some evidence to suggest that some plants can transport entire complexed forms of metals into roots (Jiang et al., 2003; Krishnamurti & Naidu, 2000). Generally, the amount of free Cd^{2+}, its soluble complexes and the capacity of the soil to replenish or buffer the concentration of dissolved Cd^{2+} largely governs the biological activity of Cd. Environmental variables that control the distribution between the solid- and solution-phase species of Cd are critical for determining the extent to which it accumulates in plants. This distribution is often controlled by the total amount of Cd in the soil, the physical factors that control the equilibrium between dissolved and absorbed species (*e.g.* soil moisture and bulk density), chemical parameters influencing the reactions that Cd can undergo (*e.g.* pH, organic matter, other cations and concentration of binding ligands), biological factors (*e.g.* plant exudates, microbial activity), climatic conditions and soil management (Gray & Mclaren, 2006; Gray et al., 1999d; McLaren et al., 1998; McLaughlin et al., 2011). This suggests that there exists a large continuum in the proportion of soil Cd available for uptake by a receptor organism that is likely to depend on the nature of organisms and the perturbations imposed by the environment (Vig et al., 2003). Therefore, it is important to investigate environmental factors that play a key role in determining the variability in soil Cd and its accumulation in specific crops. This will help develop a better understanding of the behaviour of Cd in soils and options for managing the elevated Cd concentrations in NZ agricultural soils.

1.2 Aim and objectives

The overall aims of this study were to assess the risk of the induced Cd contamination by P fertiliser application to agricultural systems and develop soil management strategies for reducing Cd accumulation in potatoes and wheat. The objectives of this thesis were to:

(1) review existing research on soil Cd in New Zealand,

(2) investigate the distribution of Cd concentrations in soils and different cultivars of lettuce, spinach, onion, potato and wheat in cropping systems and assess the influence of environmental factors in determining the Cd accumulation in these plants,

(3) investigate the effectiveness of different amendments on reducing Cd accumulation in specific crops under different field conditions, and

(4) assess possible changes in soil Cd concentrations in agricultural systems across NZ, under different types of land-use and irrigation rates, with current fertiliser management strategies.

1.3 Thesis structure

This thesis consists of nine chapters, including: General introduction (Chapter 1), Literature research (Chapter 2), Experimental research (Chapter 3 - 4 and chapter 6 - 8), Modelling research (Chapter 5) and Conclusion (Chapter 9).

Chapter 1 introduces the topic and briefly reviews the risk of Cd on health, its chemical behaviour in soils, the environmental factors determining its accumulation in plants and remediation methods in agricultural systems, and states the objectives of this thesis.

Chapter 2 reviews the current literature associated with soil Cd contamination in NZ agricultural systems, including the distribution of soil Cd concentration, environmental factors related to its distribution, mass balance, accumulation rates and remediation techniques applied in NZ.

Chapter 3 reports experimental research investigating the Cd concentration in cropping soils and plants, different methods in estimating soil Cd bioavailability and environmental factors influencing its accumulation in plants.

Chapter 4 reports experimental research evaluating the application of lime and compost (with different rates) on Cd accumulation in wheat grain and potato tuber under field trial conditions.

Chapter 5 reports modelling research that seeks to estimate the effects of P application rates, Cd concentration in P fertiliser, irrigation rate, and environmental variables (including soil pH, organic C concentration and soil bulk density) on soil Cd accumulation over the next 25 years.

Chapter 6 is a journal article published in *Science of The Total Environment* which shows the results of a field survey investigating the concentrations of Cd in onions, lettuce and spinach and analysis of their relationships with cultivar effects and the paired soil variables.

Chapter 7 is a journal article published in the *Journal of Environmental Quality* which describes the effects of cultivars and soil properties on Cd concentration in wheat under field conditions.

Chapter 8 is a journal article published in the *New Zealand Journal of Crop and Horticultural Science* which details the distribution of Cd concentrations in 10 commercial potato cultivars and assesses the effects of soil factors on Cd concentrations in two common cultivars.

Chapter 9 is the conclusion of the thesis. It provides an overview of the main findings and makes some suggestions for further study.

Chapter 2

Cadmium accumulation in New Zealand agricultural soils: a review of 40 years of research.

2.1 Introduction

Agriculture plays a central role in the New Zealand (NZ) economy. It occupies almost half of the national land area and contributes to two thirds of the total national export revenue (The Secretariat of New Zealand, 2015). Intensive farming has contributed to a large amount of fertiliser application. For example, in 2011 *ca.* 356,000 tonnes of nitrogen (N), 148,000 tonnes of phosphate (P), and 88,000 tonnes of potassium (K) fertilisers were consumed in NZ (Fertiliser Association of New Zealand, 2015). The levels of contaminants in N, S and K fertilisers are generally negligible, but their concentrations in P fertilisers are documented at high levels in some studies, particularly Cd and fluorine (F) (Loganathan et al., 2003; McLaughlin et al., 1996). Compared to other heavy metals including arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), and vanadium (V) introduced from P fertilisers, Cd is the element of most concern due to its significantly negative effects on human health (Mortvedt, 1996).

Phosphate fertilisers contain Cd at concentrations varying from negligible levels to over 500 mg Cd kg^{-1} P, depending on the phosphate rock used for its manufacture (Bramley, 1990; Kelliher et al., 2017). After introduction to agricultural systems, Cd from fertiliser application is subject to being retained by soil particles. When the rates of input are higher than those of removal, Cd can accumulate in soils over time. Long-term P fertiliser application has elevated soil Cd concentration in many countries, such as Australia (McLaughlin et al., 1996), Argentina (Giuffréde López Carnelo et al., 1997), the United States (Holmgren et al., 1993) and the European countries (Smolders & Mertens, 2013). In most agricultural soils, the soil Cd accumulation is primarily controlled by the P application rate and the Cd concentration in P fertiliser (Kelliher et al., 2017). Therefore, the reduction of P application rate or the decline of Cd concentration in fertilisers can reduce the amounts of Cd entering soils and lower its accumulation rate (Mortvedt, 1987; Richards et al., 1998; Six & Smolders, 2014).

Farmers in NZ have applied P fertilisers since the late 19th century to support the development of commercial farming. More than 100 years of P fertiliser application has resulted in the accumulation of Cd in some agricultural soils (Cavanagh, 2014; McDowell et al., 2013; Roberts et al., 1994; Taylor, 1997). As concerns about soil Cd have been raised, extensive research on Cd has been conducted in

New Zealand during the last 20 years. A literature search of www.scopus.com on 8th March, 2019 using the search terms “Cadmium”, “Soil” and “New Zealand” found 65 peer-reviewed articles related to soil Cd that had been published by NZ researchers. These studies mainly focus on soil Cd accumulation and the determinant factors (Kelliher et al., 2017; McDowell et al., 2013; Salmanzadeh et al., 2016; Stafford et al., 2018c), soil Cd bioavailability and its effects on plants and animals (Gray & Mclaren, 2006; Gray et al., 1999a, 1999d; Lee et al., 1996; Loganathan et al., 1999), and soil Cd mitigation strategies (Al Mamun et al., 2016; Al Mamun et al., 2017; Robinson et al., 2005; Simmler et al., 2013; Valentinuzzi et al., 2015). The studies on Cd up to the late 2000s were reviewed by Loganathan et al. (2003) and Loganathan et al. (2008) respectively. These two reviews focused on the chemical behaviours of Cd and its implications in pasture systems. From the late 1990s, the phasing out of Cd-rich phosphate rock has resulted in the reduction of national net Cd accumulation rate (Rys, 2011). In the last 10 years, some recent studies have reported that Cd concentrations are no longer increasing in many NZ soils (Abraham et al., 2016; Salmanzadeh et al., 2017a; Taylor et al., 2017), or in some cases, a decrease has been observed (McDowell, 2012; Schipper et al., 2011) while others argue that Cd continues to accumulate, especially in dairy systems (Kelliher et al., 2017; Stafford et al., 2018c). There was a lack of available literature research to update the information of studies on Cd and analyse these divergent results. Therefore, the aim of this study was to review the body of existing research on Cd in NZ to understand the soil Cd mass balance. It sought to meet this aim by fulfilling the following objectives: (1) evaluate the current status of soil Cd concentrations in NZ; (2) analyse the variables that have been linked to Cd enrichment in NZ agricultural soils.

2.2 Cadmium in New Zealand soils

2.2.1 Naturally occurring cadmium concentrations

The background concentrations of Cd in NZ soils are generally low (Cavanagh, 2014). A national survey of non-agricultural NZ top soils found a geometric distribution of Cd concentrations ranging between 0.02 – 0.77 mg kg^{-1}, and an arithmetic mean value of 0.2 mg kg^{-1} (n = 86). A subsequent national soil survey was conducted in 2008 where 375 background top soils were collected, covering native bush, forestry, parks, tussock, and “unfertilised land” by the Cadmium Working Group (2008). They determined an average soil Cd concentration of 0.16 mg kg^{-1}, with 99% of the measured concentrations below 0.6 mg kg^{-1}. The results from this survey were subsequently used to set the tier 1 trigger value in the Tiered Fertiliser Management System (TFMS), which was implemented to manage the possible risks from Cd accumulation in NZ agricultural soils (see Section 2.6). Similar results were reported later by McDowell et al. (2013) who estimated a mean value of 0.14 mg kg^{-1} (n = 289), and Cavanagh (2014) reported the average Cd concentration in unfertilised soils at 0.13 mg

kg^{-1} (*n* = 218), with notable differences in the ranges between the different NZ *Soil Orders* (Figure 2.1; NZ soil group names defined by Hewitt, 2010).

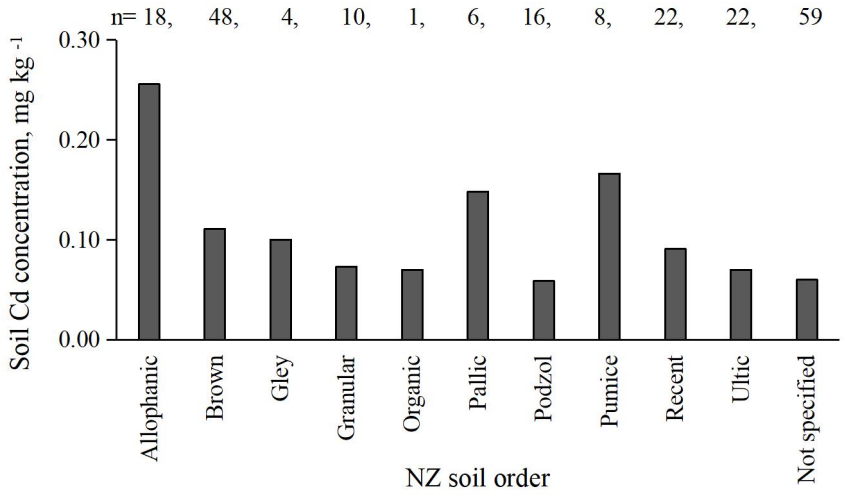

Figure 2.1 Average soil Cd concentrations in unfertilised soils divided according to NZ Soil Order. The data in this figure was from the NZ fertiliser association (Cavanagh, 2014).

2.2.2 Contamination in agricultural soils

The first national survey specific to NZ pastoral soils found that the average soil Cd concentration was 0.44 mg kg^{-1}, more than two-fold the background concentration (Roberts et al., 1994). Subsequent soil surveys were conducted by regional councils, the fertiliser industry, and research organisations, and results were reported by the Cadmium Working Group (2008), McDowell et al. (2013), Cavanagh (2014) and Abraham et al. (2016) showing that the average soil Cd concentrations range between 0.32 - 0.43 mg kg^{-1}. Cavanagh (2014) suggested that some of the variations arose from differences between detection methodologies, samples sizes and sampling periods used to estimate the 'total' soil Cd concentrations.

The geo-accumulation index (I_{geo}), developed by Muller (1969), has been widely used in assessing heavy metal pollution in sediments and soils (Dotaniya et al., 2017; Šefčík et al., 2008; Shafie et al., 2013; Wei & Yang, 2010). This index provides some description of contamination levels by categorizing it into seven classes, ranging from Class 0 (I_{geo} = 0, unpolluted) to Class 6 (I_{geo} > 5, extremely polluted). Using the I_{geo} (see Table 2.1) shows that the Cd contamination level in NZ agricultural soils can be categorized as *uncontaminated to moderate* (I_{geo} values: 0.54 – 2.11; Table 2.1). By comparison to international levels, agricultural land has mean Cd I_{geo} values of 1.49 in India

(Dotaniya et al., 2017), 1.08 in China (Wei & Yang, 2010), 0.90 in Slovakia (Šefčík et al., 2008), while industrially contaminated site have higher values, such as 4.8 in a Zn mining area (Du et al., 2008).

Table 2.1 Average and range of soil Cd concentration (mg kg^{-1}) and contamination levels in some NZ top-soils.

Soil sample depth (cm)	Land use	Unfertilised soil			Fertilised soil			I_{geo}	Reference
		Mean	Size	Range	Mean	Size	Range		
0 - 7.5	Pasture	0.20	86	0.02 – 0.77	0.44	312	0.04 - 1.53	0.55	(Roberts et al., 1994)
0 - 10 & 0 - 15	Agricultural	0.16	375	<0.01 – 0.77	0.35	1794	<0.01 - 2.52	0.54	(Cadmium Working Group, 2008)
0 - 20	Agricultural (Waikato only)	0.11	36	<0.01 – 0.30	0.71	215	0.10 - 2.00	2.11	(Taylor et al., 2010)
0 - 10	Agricultural	0.14	289	<0.01 – 0.67	0.32	939	<0.01- 2.70	0.61	(McDowell et al., 2013)
	Agricultural				0.44	3700	<0.01 - 2.14	1.17	
	Cropping				0.28	505	0.03 – 2.04	0.52	
0 - 7.5 & 0 - 10	Dairy	0.13	218	<0.01– 0.90	0.59	1841	0.04 – 2.14	1.60	(Cavanagh, 2014)
	Drystock				0.33	1255	0.05 – 2.05	0.76	
	Orchard				0.55	87	0.05 – 2.10	1.50	
0 - 10	Pasture	--	--	--	0.89	69	0.25 - 1.58	--	(Reiser et al., 2014)
0 - 7.5 & 0 - 10	Agricultural	--	--	--	0.43	6840	<0.01 - 3.05	1.14	(Abraham et al., 2016)
0 - 30	Pasture (Otago and Southland)	0.028	43	0.005 – 0.24	0.097	241	0.005 – 1.31	1.21	(Martin et al., 2017)

Note: The geo-accumulation index, I_{geo} was calculated as $I_{geo} = \log_2 (C_n / 1.5\ B_n)$, where C_n is the measured concentration of soil Cd in the environment, *Bn* is the soil geochemical background value. In this study, the mean Cd concentration of unfertilised soil at the same row was used as the background value in the I_{geo} calculation. The I_{geo} for Cd is classified as: uncontaminated ($I_{geo} \leq 0$); uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderately to heavily contaminated ($2 < I_{geo} \leq 3$); strongly contaminated ($3 < I_{geo} \leq 4$)). In this study, the I_{geo} was calculated by the mean Cd concentration of fertilised soils and the mean value of non-fertilised soils in the same row.

At a regional level in NZ, the highest average Cd concentrations have been measured in the Waikato regions (Figure 2.2). According to soil Cd concentration reported by (Taylor et al., 2010), the soil Cd contamination in Waikato was *moderate* (I_{geo} value of 2.11) when the mean Cd concentration in unfertilised soils (0.11 mg kg^{-1}) was employed as background values. Morton and Roberts (2017) reported the average soil Cd concentration on a 102 ha Waikato dairy farm at 1.36 mg kg^{-1} (top 7.5 cm), which was within *heavy* Cd contamination levels (I_{geo} = 2.80). In contrast, Canterbury, Otago, Southland and Wellington regions were found to have the lowest average soil Cd contamination with I_{geo} values of < 1.00 against their region-specific Cd concentrations in unfertilised soils, based on the data provided by the NZ fertiliser association (Cavanagh, 2014).

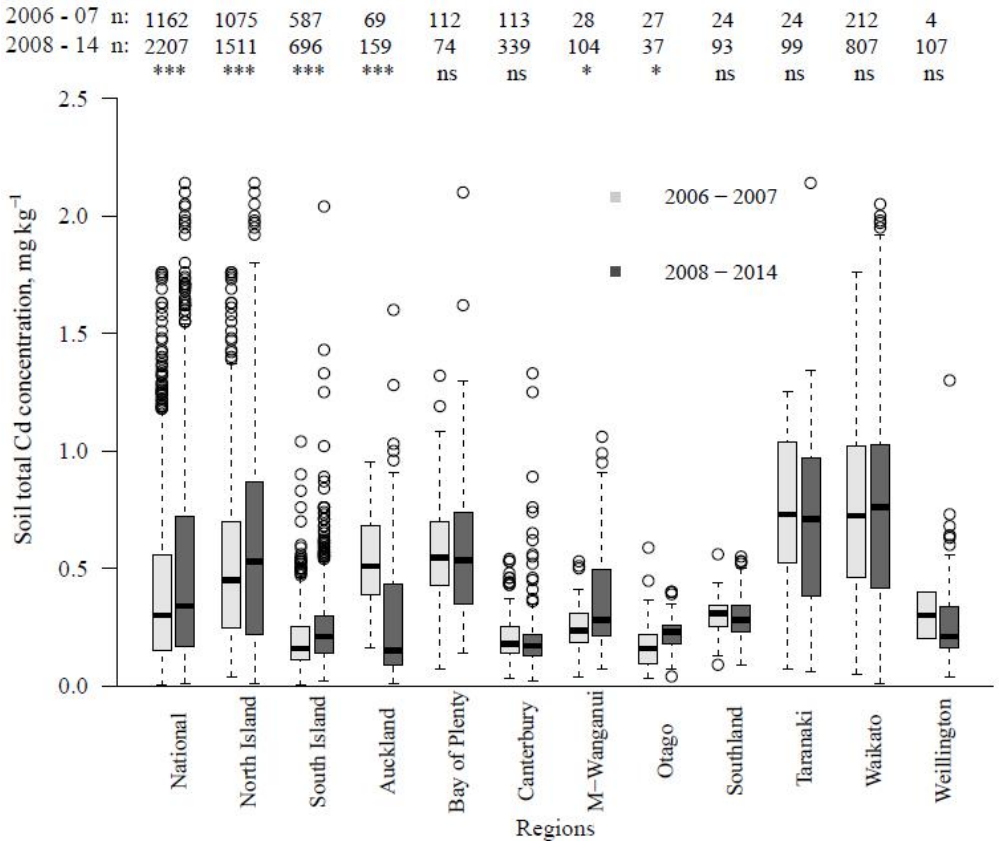

Figure 2.2 Boxplots of Cd in agricultural soil according to regions showing median, 25th and 75th quartiles and the 5th and 95th percentiles as whiskers and the circles as outliers. The number of asterisks, ***, ** and * show a significant difference at the $P < 0.001$, $P < 0.01$ and $P < 0.05$ level respectively, while ns means no significance according to a Mann-Whitney test for soil Cd concentrations between two periods. The data in this figure was from the NZ fertiliser association (Cavanagh, 2014).

The type of land use has been found to be an important determinant of soil Cd concentrations (Cadmium Working Group, 2008; Cavanagh, 2014; McDowell et al., 2013). Cavanagh (2014) showed that soils from dairy and orchard farming systems had higher I_{geo} values (1.60 and 1.50, respectively)

than those from drystock (0.76) and cropping (0.52) systems. National soil Cd data collected from 2008 to 2014 also indicate that soils used for dairy farming had the highest median Cd concentration (0.59 mg kg^{-1}), significantly higher than those for drystock (0.25 mg kg^{-1}), orchard (0.25 mg kg^{-1}) and cropping farming (0.23 mg kg^{-1}) (Figure 2.3A), while soils that were not used for agriculture had the lowest median concentrations (0.07 mg kg^{-1}). If taking this value (0.07 mg kg^{-1}) as the background concentration, the calculated value of I_{geo} for dairy soil is 2.01, which means that Cd contamination in dairy systems falls into the *moderate to heavy* range.

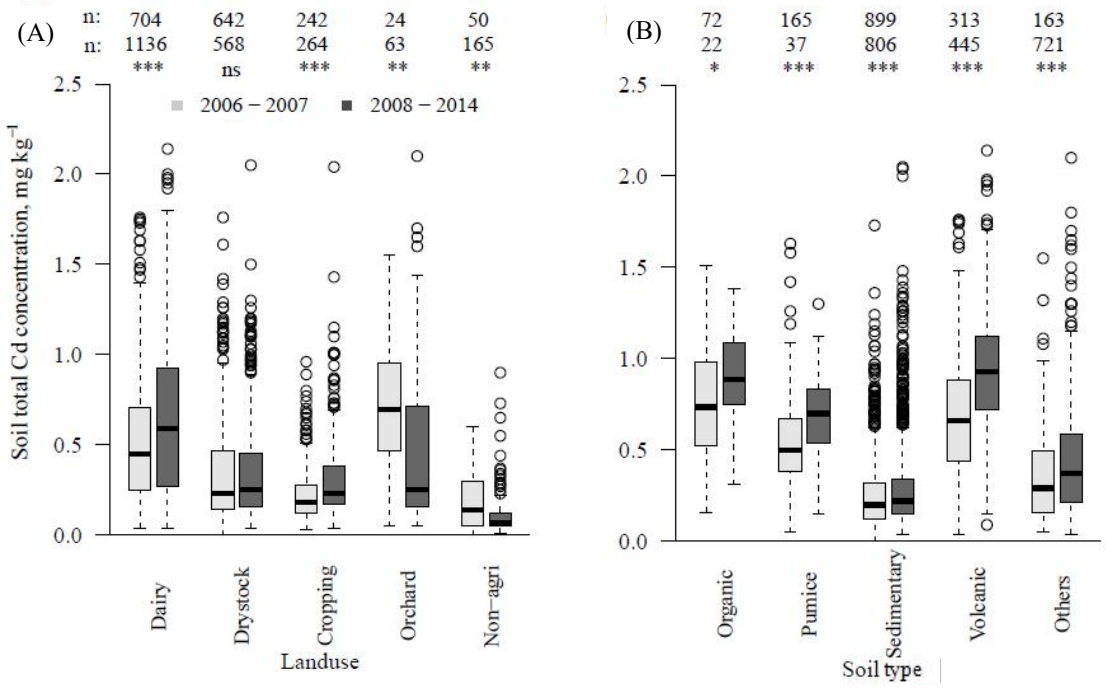

Figure 2.3 Boxplots of Cd in agricultural soil according to (A) landuse and (B) soil type showing median, 25th and 75th quartiles and the 5th and 95th percentiles as whiskers and the circles as outliers. Soils not belonging to the four main soil orders were considered as Others in this study. The number of asterisks, ***, ** and * show a significant difference at the $P < 0.001$, $P < 0.01$ and $P < 0.05$ level, respectively, while ns means no significance according to a Mann-Whitney test for soil Cd concentrations between two periods. The data in this figure was provided by the NZ fertiliser association (Cavanagh, 2014).

2.2.3 Implications of high soil Cd concentrations

Elevated soil Cd concentrations in NZ are not believed to threaten human health and is unlikely to significantly affect ecosystems (Cadmium Working Group, 2008; Cavanagh et al., 2013). However, the risks of the exceedance of food standards in some plants and animal organs exist, especially in

some high Cd soils. Since the 1990s a large amount of research in NZ has been carried to investigate the transfer of Cd from soil to plants. These studies mainly covers human food crops, such as wheat, potato, carrot, onion, and lettuce, and pastoral plants such as ryegrass and white clover (Appendix Table A1).

Gray et al. (1999a) grew lettuce in ten soils with Cd concentrations ranging from 0.03 to 1.34 mg kg^{-1} and found that Cd concentrations in 30% of lettuce samples were higher than 2 mg kg^{-1} (dry weight, DW) with the highest value at 4.50 mg kg^{-1}. These were higher than the maximum limit in the Food Standard of Australia and New Zealand (FSANZ, 0.1 mg kg^{-1} (fresh weight, FW)) assuming a normal 95% moisture content. In another pot experiment conducted by Gray et al. (1999c), lettuce Cd concentrations were reported at 3.95 mg kg^{-1} (DW) when soil pH was maintained at 5.5. For wheat which is a staple horticultural crop with the largest harvested area in NZ, Gray et al. (2001) showed that 10% of 391 wheat grain samples exceeded the 0.1 mg kg^{-1} (FW) guideline value. On a regional scale, mid-Canterbury is traditionally a major wheat-growing zone in NZ which is dominated by sedimentary soils with normally low soil pH and OC content (Pallic and Brown soils in Table 2.2). Cavanagh et al. (2016) estimated that if the soil Cd concentrations in Canterbury increased by factors of 1.3 - 1.4 times, the high bioavailability of soil Cd would result in wheat with the most potential to exceed food standards for Cd. Kim (2005) found that the mean Cd value of potato samples (another important staple food crop) was 0.025 mg kg^{-1} (FW) in the Waikato, with around 1.5% of the potato samples higher than the maximum limit of current food standard.

Cadmium in animal tissue is mainly concentrated in the kidneys and livers (Bramley, 1990; Lee et al., 1996; Roberts et al., 1994). Lee et al. (1996) also showed that for fleece-free sheep over the first 3-month grazing period, 50 - 67% of the total accumulated Cd was distributed in kidneys and livers, followed by muscle (6 - 26%) and the digestive tract (16 - 25%). Data from the national survey conducted by Roberts et al. (1994) between 1988 and 1991 indicated 22 - 28% of sheep and 14 - 20% of cattle kidneys samples had Cd concentrations exceeding the maximum permissible concentration of 1.0 mg kg^{-1} (FW). To attempt to meet the European Communities import requirements, an offal-discard policy set up in the 1990s was that kidneys from sheep older than 30 months should be banned from the human food chain. From 2002, new standards for Cd on animal organs were applied (0.05 mg kg^{-1} for fresh muscle, 2.50 mg kg^{-1} for kidneys and 1.25 mg kg^{-1} for livers) in NZ (Loganathan et al., 2008). As a result, the change in standards (increased the limit from 1 mg kg^{-1}) dropped the proportion of the samples that exceed the Cd limits in animal offal greatly. Based on Cd concentrations in plant and soil through a pastoral survey, Reiser et al. (2014) modelled the amount

of daily intake of Cd for grazing animals and estimated that Cd concentrations in 2.9% of cow and 1.4% of sheep kidneys and 2.9% of sheep livers could exceed the current maximum permitted values.

Apart from the direct risk from the exceedance of food standards on human health, high soil Cd concentrations can restrict the use of certain types of lands. In many counties, Cd limits in agricultural soils have been proposed, 0.4 mg kg^{-1} in Japan (rice land) (Makino et al., 2016), 3.0 - 6.0 mg kg^{-1} in India (Bhatti et al., 2016) and 1.0 mg kg^{-1} in Northern China (Ji et al., 2012). The soils with Cd concentrations exceeding this permissible threshold should be phased out of cropping purposes or replaced by non-food crops, for example, bioenergy plants. In NZ, there are no specific permissible soil Cd concentrations in cropping and pastoral farming systems. In TFMS, for soils with Cd concentration $\geq$ 1.8 mg kg^{-1}, no further Cd accumulation is permitted unless a site-specific risk assessment is conducted. Additionally, in the National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health (NES) which were developed to manage the risk of soil certain contaminants, a soil Cd limit of 0.8 mg kg^{-1} for rural residential landuse was set under the most restricted situation, based on the relationship of soil variables (soil pH and total Cd concentration) and Cd uptake by plant (Ministry for the Environment, 2011). This means that a considerable amount of NZ agricultural soils have been higher than this Cd soil contaminant standard. The exceedance of the national environmental standard in some soils limits their flexibility for landuse purposes.

2.3 The effect of environmental variables on soil Cd accumulation in NZ

2.3.1 Soil chemical properties and soil type

Cd sorption is often the dominant reaction in agricultural soils, due to the relatively low soil solution Cd concentrations and the existence of binding sites on soil surfaces (Loganathan et al., 2012; Rieuwerts et al., 1998). The soil constituents mainly associated with Cd sorption are layer silicate clays, organic matter and metal oxides (Gray et al., 2000; Loganathan et al., 2012). In NZ, Gray et al. (1998) tested six lime-amended soils with pHs ranging between 4.9 and 6.2 in the laboratory and found the sorption of added Cd (2.0 mg kg^{-1}) increased with pH from 38% to 96%. They went on to develop statistical models that considered a range of soil chemical variables (total Cd and organic carbon (OC), Olsen & total P, soil texture, CEC and metal oxides) and found that soil pH and OC could explain 87% of the variation in Cd sorption on those soils. A subsequent study of 29 NZ soils spanning 10 out of 15 NZ soil orders, with widely ranging soil properties (including OC, pH, free oxides and clay minerals), showed that soil pH, OC and total Cd significantly correlated with $Ca(NO_3)_2$ extracted Cd (R^2 = 0.763) (Gray et al., 1999d). Soil pH, OC and total Cd content could also predict

water-soluble soil Cd concentrations, albeit with less precision ($P < 0.001$, $R^2 = 0.50$) (Gray & Mclaren, 2006). These are consistent with the findings in some overseas studies indicating that soil pH and organic matter concentration are the dominant factors in determining soil Cd bioavailability (Loganathan et al., 2012; Six & Smolders, 2014). The effects of pH on Cd adsorption/desorption in soils include: (1) the effects on soil negative surface charge of soil colloids; (2) the alternation of hydroxyl species of Cd in solution; and, (3) the dissolution of inorganic ligands, such as $CdCl^+$, $CdSO_4^0$ at low soil pHs or the soluble organo-metal complexes at high soil pHs (Smolders & Mertens, 2013). In a narrow pH range ("the sorption edge", pH 4 – 8), Cd sorption by soil is sensitive to pH and increases rapidly with increasing pH (Loganathan et al., 2012). The influence of organic matter on Cd bioavailability is likely due to functional groups, such as carboxyl (COOH–), phenolic (–OH) and sulfhydryl (–SH) groups, which bind Cd through ion exchange, precipitation or forming stable organometallic complexes in soils (Loganathan et al., 2012). Gray et al. (2000) showed that up to 34% of soil Cd could be associated with the organic soil fractions, with a further 38% in the 'residual fraction' that could only be extracted with concentrated HNO_3. Based on this, Al Mamun et al. (2016) found that compost application could decrease the concentrations of Cd by more than 20% in onions, spinach and lettuce in two NZ soils. In the Acid-Base theory, Cd^{2+} is considered as a 'soft' Lewis acid while Zn^{2+} and Ni^{2+} are 'hard' Lewis acids, and hence Cd^{2+} is likely to show a greater affinity to soft Lewis bases in organic matter (typical -SH and -NH_2 groups) than hard Lewis acids (–COOH and –OH groups) (Alloway, 1990). Using this chemical property, Welikala et al. (2018) compared the effects of ten different NZ local solid organic C-rich substrates on the Cd, Ni and Zn bioavailability, and suggested that compost could be a suitable amendment to reduce soil available Cd without inducing Zn deficiency.

The affinity for NZ soils with relatively high Fe and Al mineral contents to bind phosphate has been recognized for over five decades (e.g. Saunders, 1965), and consequently these soils require greater phosphate fertilizer inputs to maintain productivity. Moreover, soils where these minerals are abundant are also known to stabilize organic matter and bind Cd (González-Costa et al., 2017; von Lützow et al., 2008). This is reflected in national soil surveys showing relatively high Cd concentrations in some NZ volcanic soils (Cavanagh, 2014; McDowell et al., 2013; Roberts et al., 1994). These studies also highlighted the strong retention of Cd by *Organic Soils* (defined as having either 30+ cm depth of peat or 40+ cm of forest litter (Hewitt, 2010)). According to the survey of soils collected by NZ fertiliser association from 2008 to 2014, Volcanic soils had the highest Cd concentrations (0.93 mg kg^{-1}), followed by Organic soils (0.89 mg kg^{-1}), which were also significantly higher than Pumice (0.70 mg kg^{-1}) and Sedimentary soils (0.22 mg kg^{-1}) (Figure 2.3B) (Cavanagh, 2014). This trend is further illustrated by comparing the ratio of $Ca(NO_3)_2$ - extractable Cd to total Cd

across different soil orders: the extractable fraction of Cd in sedimentary soils (0.174 - 0.293) is generally higher than in volcanic ash soils (0.046 - 0.074) (Table 2.2). Of particular interest in NZ is the abundance of allophane (a hydrous aluminium silicate clay mineraloid with amorphous/poorly crystalline structure) in some volcanic soils (*i.e. Allophanic Soils* (Hewitt, 2010)), which has a high affinity for phosphorus (Parfitt, 1990). Bolan et al. (2003a) reported allophanic soils had higher pH and greater amounts of negative charge and Cd^{2+} absorption compared to non-allophanic soils. Stafford et al. (2018c) investigated two dairy farms in Canterbury and Waikato with different P application histories and found a significant positive correlation between soil Cd and total C and N, CEC and P retention. They measured greater Cd concentrations in the Waikato soils with higher amounts of organic matter, allophane and Fe/Mn-oxide minerals, while relative organic matter contents reflected the different soil Cd concentrations on the Canterbury farm. The differences in soil Cd concentrations between regions were linked to historic P fertiliser use, while soil characteristics were important in determining variability within the individual farm (Stafford et al., 2018c).

Table 2.2 Summary of the studies on plant and extractable Cd with the identification of soil order.

Soil order [a]	Plant				Extractable Cd [d]	
	Wheat Cd [b] (mg kg^{-1})	Cd_{plant}: Cd_{soil} ratio	Ryegrass Cd [c] (mg kg^{-1})	Cd_{plant}: Cd_{soil} ratio	0.05 M $Ca(NO_3)_2$ (mg kg^{-1})	Cd_{sol}: Cd_{soil} ratio
Allophanic	0.269	0.319	0.250	0.242	0.037	0.056
Brown	0.185	1.047	0.135	1.429	0.727	0.174
Gley	0.094	0.545	0.166	1.455	0.011	0.074
Granular	0.150	0.192	0.588	0.754	0.036	0.046
Organic			0.054	0.377		
Pallic	0.072	0.549	0.287	0.470	0.301	0.176
Pumice	0.186	0.410	0.164	0.364	0.038	0.075
Recent	0.151	0.795	0.236	1.240	0.708	0.293

Note: [a] Cd concentrations in wheat grain, ryegrass and 0.05 M $Ca(NO_3)_2$ extraction have been reported under various soil types in some studies, which are used to represent for the bioavailability of soil Cd here.
[b] The mean values of wheat Cd concentrations were calculated using data from Gray et al. (1999c), Gray et al. (1999a), Gray et al. (2001) and Black (2010).
[c] ryegrass values from Gray et al. (1999c), Gray et al. (1999a), Gray and McLaren (2005), Gray and McDowell (2016), Simmler et al. (2013) and Stafford et al. (2016).
[d] The information summarized from research that measured 0.05 M $Ca(NO_3)_2$ extractable Cd (Black, 2010; Gray et al., 2003b; Gray et al., 1999a, 1999c; Simmler et al., 2013).

In soil solution, free Cd^{2+} and most of its soluble complexes can be considered as the immediately bioavailable pool, although its amount may be negligible (Taylor & Percival, 2001). For a pH neutral uncontaminated soil with total Cd concentration of 2 mg kg^{-1}, soil solution Cd concentrations generally vary between 0.1 and 5 µg L^{-1} (Smolders & Mertens, 2013). In general, the amount of free Cd^{2+} and its soluble complexes largely govern the amount of Cd lost via leaching or plant offtake, which negate soil Cd accumulation. Hence, environmental variables that control the equilibrium between the solid- and solution-phase species of Cd are critical for determining the extent to which it accumulates in soils. Apart from the soil variables (such as soil pH, organic C, CEC) mentioned above, the formation of stable dissolved Cd complexes with inorganic ligands can also shift the equilibrium towards the dissolved phase. Probably the best known of these in NZ is the dissolved chloride ion (Cl^-) which is known to form relatively stable Cd-Cl complexes ($CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, $CdCl_4^{2-}$) and thus increase the solubility of Cd in soil solutions. In a simulated centre-pivot irrigation experiment with three treatments (superphosphate, dairy shed effluent and cow urine), Carrick et al. (2014) found that dairy cow urine deposition markedly increased the amount of Cd leaching. They concluded that due to the high amount of Cl, urine is the key factor determining Cd leaching. Similar results have been obtained by Gray et al. (2017b). The greater amounts of urine inputs cause significantly larger Cd fluxes ($P < 0.05$) by increasing Cd concentration in drainage. They suggested

that the amount of Cl inputs via urine deposition was the main reason for the difference of Cd lost between 24-h grazed plots and the 6-h plots.

2.3.2 Biotic effects

Cadmium can be removed from soil through crop offtake, while the amount of Cd uptake by plants varies between plant species (Table 2.3; Appendix Table A1). The average Cd concentrations in lettuce across all studies in NZ is 1.25 mg kg^{-1} (DW), followed by carrot root (0.62 mg kg^{-1}), while wheat has the lowest Cd concentration (0.08 mg kg^{-1}) (*c.f.* Table A1 in Appendix, and references therein). Overall, Cd accumulation in plant species generally has followed the order: leafy vegetables > root vegetables > grain crops >fruit (Cadmium Working Group, 2008). For animal forage, the average ryegrass and clover Cd concentrations were 0.288 and 0.122 mg kg^{-1} (DW) respectively, two to ten times lower than chicory and plantain which are used as forage herbs in NZ (Table 2.3). The data from field surveys also confirms that the Cd concentrations in ryegrass and clover plant tissue are low when compared to weed species. The differences between cultivar varieties in uptake of Cd are also well studied in some plants. For example, Gray et al. (2001) investigated the relationship of wheat grain Cd concentration with various variables such as soil properties and cultivar difference. The results that wheat grain Cd concentrations average at 0.06 mg kg^{-1} with a range from 0.013 to 0.250 mg kg^{-1} (dry weight) indicated that different cultivars, rather than soil properties, contributes to a considerable variation of grain Cd concentration. Similar studies on cultivar variety were also conducted on poplar (Robinson et al., 2005), willow (Robinson et al., 2005), ryegrass (Cavanagh et al., 2016; Gray & McLaren, 2005), potatoes (Ashrafzadeh et al., 2017; Cavanagh et al., 2016) and onion (Cavanagh et al., 2016). Apart from the direct Cd removal from soil, forage plant species can also be important in the amount of daily animal Cd intake. Stafford et al. (2016) modelled Cd intake by sheep when feeding them with different forage crops for 30 days. Compared to perennial ryegrass-white clover pasture, they found that chicory monoculture and chicory-white clover mixed forage intake could increase kidney Cd concentrations to 2.23 and 1.28 mg kg^{-1} (fresh weight), respectively, whereas a feeding on perennial ryegrass-white clover pasture was unlikely to result in significant Cd intake. Others have found that Cd intake from pasture is likely to account for 70-80% of total Cd intake for cows and sheep while the effect of soil digestion on Cd accumulated in the animal body is negligible (Lee et al., 1996; Reiser et al., 2014).

Table 2.3 Summary of Cd concentrations in plants and paired soils in NZ (mg kg^{-1}, DW).

Plants	Soil Cd			Plant Cd		
	N	Mean	Range	N	Mean	Range
Pasture—field survey						
Grass [a]	312	0.44	0.04 - 1.53	312	0.10	0.04 - 0.17
	24	0.34	0.25 - 0.49	24	0.26	0.17 - 0.35
Legume [b]	312	0.44	0.04 - 1.53	312	0.06	0.03 - 0.07
	24	0.34	0.25 - 0.49	24	0.28	0.14 - 0.54
All pasture [c]	69	0.89	0.25 - 1.58	69	0.13	0.01- 1.55
Pasture in pot or field trial experiments						
Ryegrass [d]	26	0.55	0.03 - 3.20	101	0.29	0.03 - 0.85
Clover [e]	47	0.35	0.03 - 1.34	53	0.12	< 0.01 - 0.97
Plantain [f]	8	0.51	0.13 - 0.79	12	0.60	0.21 - 0.99
Chicory [g]	8	0.52	0.13 - 0.79	8	1.34	0.35 - 1.96
Crops in pot or field trial experiments						
Wheat [h]	45	0.24	0.03 - 1.34	94	0.08	0.02 - 0.59
Lettuce [i]	27	0.35	0.03 - 1.50	37	1.25	0.08 - 1.50
Potato [j]	5	0.55	0.06 - 1.45	38	0.13	0.01 - 0.45
Onion [k]	9	0.72	0.13 - 1.50	10	0.12	0.04 - 0.22
Carrot (root) [l]	13	0.36	0.03 - 1.34	19	0.62	0.12 - 1.91
Maize [m]	10	0.36	0.03 - 1.34	10	0.21	0.01 - 0.67

Note: [a, b] Field survey data sourced from Roberts et al. (1994) and Roberts and Longhurst (2002), and [c] from Reiser et al. (2014). [d - m] Pasture and crop Cd information in pot or field trial experiments were summarized from relevant research conducted in NZ listed in Appendix Table S1.

Animal behaviours, such as grazing and faeces deposition can also influence soil Cd concentration. Saggar et al. (1990) reported that 70% of total pasture production could be utilized by animals, while most animal intake Cd was returned to soils through faeces (Lee et al., 1996). Loganathan et al. (1995) found the above-ground Cd movement caused by animal grazing varied between annual losses (-29 g ha^{-1}) and accumulation (41 g ha^{-1}), which accounted for 2 - 13% of annual fertiliser Cd. In a hilly sheep-grazed farm, Roberts and Longhurst (2002) found the paddock position posed a notable effect on soil total Cd concentration. In their study, the soils sampled from animal campsites had the highest Cd concentrations (0.49 mg kg^{-1}) while steep slope areas were the lowest (0.25 mg kg^{-1}). They suggested that a larger amount of faeces deposition on animal campsites was one of the reasons for the greater Cd enrichment in this area. Apart from pasture, animals can intake Cd via soil digestion, although it may only contribute a negligible part of total Cd ingestion (Reiser et al., 2014; Roberts & Longhurst, 2002). Additionally, cow urine deposition may also be one of the animal behaviours influencing soil Cd enrichment due to the high Cl concentrations as noted in Section 2.3.1.

2.3.3 Climactic factors

When combined with warm temperatures, optimal soil moisture conditions are conducive to increased plant growth rates, with associated increased solute removal rates from soils. Loganathan et al. (1996) reported strong seasonal effects on pasture Cd concentration, where the highest growth rates in spring resulted in low herbage Cd concentrations due to dilution by the biomass. Reiser et al. (2014) investigated the effects of solar radiation, total rainfall and air temperature on soil total Cd, extractable Cd and pasture Cd concentration. Their results showed that soil total Cd concentrations correlated negatively with air temperature ($P < 0.05$), while $Ca(NO_3)_2$-extractable Cd and pasture Cd concentrations correlated positively with annual total rainfall ($P < 0.05$). They hypothesized that higher rainfall combined with soil acidity could promote Cd loss via leaching and uptake by plants. McDowell (2010) analysed Cd concentrations in soils collected from irrigated and non-irrigated plots that had been exposed to similar P fertiliser inputs at the Winchmore long-term field trial. He found that the soil Cd concentrations on the irrigated plots (moisture contents ranged between 10-20%) were approximately 20-25% lower than on the dryland plots (where average soil Cd concentration was 0.58 mg kg^{-1}). He linked the reduced concentrations to higher rates of Cd leaching, pasture off-takes and outwash from the irrigated soils. Similarly, Stafford et al. (2018a) reported that increasing soil moisture contents could increase Cd solubility. They indicated that large rainfall events in summer and autumn might promote Cd uptake by plantain.

2.3.4 Slope

Loganathan et al. (1995) investigated the soil Cd distribution in a sheep grazing hilly pasture and concluded that slope significantly affected soil Cd accumulation ($P < 0.001$). Topsoil Cd concentrations of both high and low P application trials on gentle slopes (0 - 12 ° gradient) were higher than those soils from steep slopes (> 26°) after 20+ years of single superphosphate (SSP) application. The higher Cd concentrations on the shallower slopes were attributed to the larger amounts of fertiliser input and the greater amount of Cd returned from faecal deposition of animals due to the greater amount of time spent by animals there. Roberts and Longhurst (2002) investigated the effects of paddock position on soil Cd concentrations, and found that the campsites had the highest soil Cd concentration (0.49 mg kg^{-1}) while steep slopes exhibited the lowest (0.25 mg kg^{-1}). In a long-term P fertiliser application hilly trial, soil Cd concentrations on steep (30 - 40°) slopes in all four treatments were lower than on the shallower (10 - 20°) slopes, and annual Cd accumulation rates also showed the same pattern (Figure 2.5A) (Schipper et al., 2011). Similarly, Stafford et al. (2018c) reported that soils from the steepest (15 - 25°) hilly areas of a dairy farm in the Waikato region had the lowest soil Cd concentrations, when compared to areas with gentler

gradients (<15°). Apart from the differences in P fertiliser and animal faeces input between slopes, Schipper et al. (2011) suggested that the greater amounts of loss of Cd through leaching, outwash water and particulate movement from steep slopes areas were also important processes in forming the difference.

2.3.5 Soil depth

Atmospheric deposition, fertiliser use, and herbage recycling mainly deposit Cd onto the soil surface, where it is usually retained strongly (see Section 2.1). Soil Cd concentrations in NZ have generally been found to decrease with soil depth (Cavanagh, 2014; Gray et al., 2003b; Loganathan & Hedley, 1997; Loganathan et al., 1995; Roberts et al., 1994; Salmanzadeh et al., 2016; Stafford et al., 2018b; Zanders et al., 1999). Roberts et al. (1994) showed that pastoral soils across all soil orders had a higher mean Cd concentrations in the top 2.5 cm than in the 2.5 – 7.5 cm depth, with up to a 40% decrease between the two depth ranges, while differences between the two depth ranges in native soils were small. Loganathan and Hedley (1997) subsequently showed that around 93% of the applied Cd remained within the top 12 cm. This distribution pattern with soil depth is not affected by slope (Loganathan et al., 1995), fertiliser rate and types (Loganathan & Hedley, 1997), soil order (Salmanzadeh et al., 2016) and irrigation practices (Salmanzadeh et al., 2017b). Due to this stratification in soil Cd concentrations, the influence of sampling depth on topsoil Cd concentration can be significant and has been linked to differences in soil Cd concentrations observed in different surveys (McDowell et al., 2013). Soil management practices that disturb the vertical distribution of the soil, such as inversion and/or tilling, would also redistribute the Cd. This has been shown overseas where tillage was determined to have homogenised soil Cd concentrations within the soil profile (Chen et al., 2009), and was used to explain homogeneous soil Cd concentrations with depth on a Canterbury dairy farm (Stafford et al., 2018c). With this heterogeneity in mind, a standardized sampling depth for soil Cd has been established in the TFMS as 0-150 mm (FANZ, 2016)

2.3.6 Contact time between Cd and the soil

The effect of 'aging' on inorganic soil contaminant solubility has been studied extensively worldwide, with most studies agreeing that the solubility decreases with time after contamination (Lock & Janssen, 2003; Seuntjens et al., 2001). Increasing contact time can reduce soil Cd bioavailability, and therefore lower its lost via leaching or crop offtake. Research on NZ soils supports these findings. Gray et al. (1998) showed that the extractable (*viz.* soluble) fraction of Cd decreased progressively over 70 days by up to 16-47%, with the greatest and lowest reductions in soils with high and low Mn, Fe and Al oxide contents, respectively. McLaren et al. (1998) found that the amount of Cd that

desorbed from isolated clay fractions of two NZ soils decreased with increasing contact time, with up to a 25% decrease between 1 and 16 weeks after introducing the Cd to the clay isolated from a Wakanui soil (a NZ *Pallic Soil*). However, in an experiment with much longer contact time (17 years), Gray et al. (2016) found that the contact time of Cd in soil had a non-significant effect on Cd bioavailablility tested by isotopic dilution techniques. There was no specific reason explained for the discrepancy, despite the presence of high amorphous Fe and Al oxides and soil C concentration in the tested soils, which should have provided a considerable capacity for slow reactions. Future studies involving the effects of contacting time on soil Cd were recommended to be conducted with more NZ soil types.

2.4 Soil cadmium mass balance in New Zealand

2.4.1 Cadmium input with phosphorus fertiliser

Taylor (1997) monitored the change in Cd concentrations in 58 top soils over 30-50 years and found that soil Cd concentrations increased from 0.39 to 0.85 mg kg^{-1}, with a mean annual increase of approximate 0.01 mg kg^{-1}, which they attributed the increase to P fertilizer application. Furthermore, comparing unfertilised soils (undeveloped native bush reserve), Zanders et al. (1999) concluded that the application of P fertiliser in NZ raised soil Cd loading 3-20 times. McDowell et al. (2013) used two data sets, including soil from minimally disturbed (n = 293) and anthropogenic sites (n = 1043) to systematically assess the effects of phosphorus fertiliser inputs on soil Cd accumulation. They found a linear relationship between soil total Cd and soil total P ($P < 0.001$, R^2 = 0.58). Data from a national soil survey also indicated that soils with more intensive agricultural practices (high maintenance P fertiliser demands) tend to accumulate higher concentrations of Cd (Figure 2.3A). For example, Waikato and Taranaki regions have the highest densities of dairy cattle, and have the highest numbers of dairy cows in NZ (Statistics New Zealand, 2017). The predominance and long-term intensive P application in these two regions were considered as an important reason for the highest average soil Cd concentrations compared with other NZ regions (Stafford et al., 2014) (Figure 2.2A).

Historically, the fertilisers in NZ were derived from rock phosphate sourced from Nauru, Christmas Island and North Carolina (USA) that contained Cd concentrations of up to 470 mg Cd kg^{-1} P (Cadmium Working Group, 2008). As concerns increased about the potential risk posed by high soil Cd concentration, a voluntary limit of 340 mg Cd kg^{-1} P was initially introduced in 1995, and was finally established at 280 mg Cd kg^{-1} P in 1997. As a result, in 1996, China, Togo and Morocco became the main sources of rock phosphate, with the latter being the current principal supplier. With the change in the provenance of the phosphorus, during the period between 2003-2015 the

average Cd concentration in P fertiliser had fallen to 184 mg Cd kg^{-1} P: a 62.5% decrease from the 1950s concentrations (Taylor et al., 2017). Kelliher et al. (2017) divided the history of P fertiliser use in NZ into five periods and estimated fertiliser Cd concentrations for those periods (Figure 2.4). The annual Cd input in NZ can be reduced further with the development of rock phosphate mining from the seabed at the Chatham Rise, located approximately 450 km off the east coast of NZ. The rock phosphate mined from here is believed to have a considerably lower Cd content (<5 mg Cd kg^{-1} P) than current and historic sources (Authority of New Zealand Environmental Protection, 2015; Bramley, 1990).

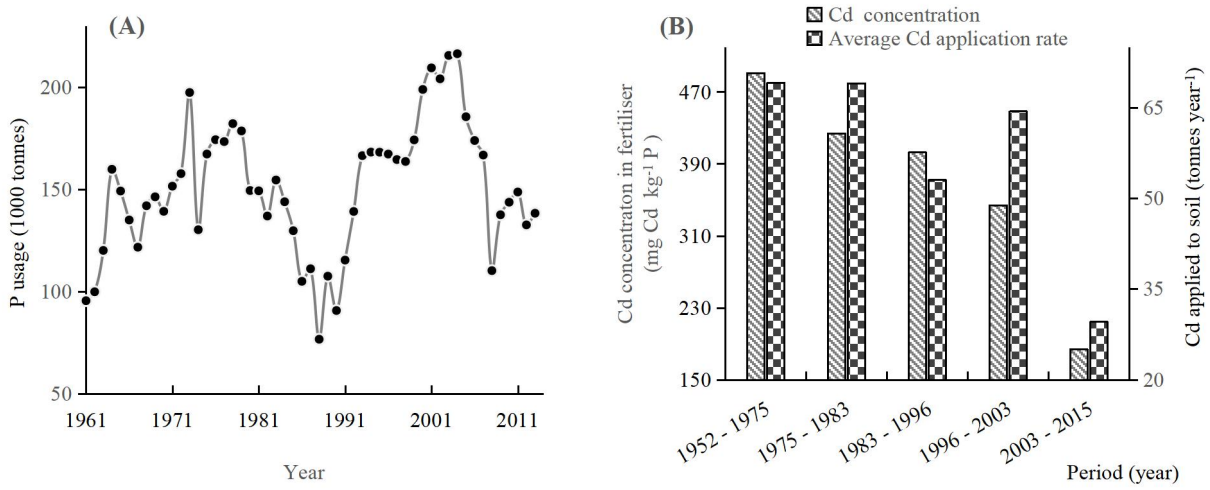

Figure 2.4 Historical trends in (A) annual P usage (1961-2014 data from Fertiliser Association of New Zealand (2015) and Journeaux (2016)) and (B) the Cd concentration in P fertiliser (Kelliher et al., 2017). The average Cd application rate for 1952-1975 is estimated by using annual P usage data from 1961 to 1975 only.

Between 1961 and 2013 the mean annual P fertiliser use in NZ was around 1,506,000 tonnes (Figure 2.4A) (Fertiliser Association of New Zealand, 2015). These annual P usage data can be used together with Cd concentrations of P fertiliser to estimate annual total Cd inputs into NZ soils. Following decreases in both the P fertiliser use and fertiliser Cd concentrations since 2003, there has been a corresponding decline in soil Cd input from 69 tonnes $year^{-1}$ in the 1950s to 30 tonnes $year^{-1}$ in the period between 2003 and 2015 (Figure 2.4B). In 2016, the land area being used for agricultural proposes in NZ was 12.1 million ha (Statistics New Zealand, 2017), so the average Cd input rate into agricultural soils was about 2.5 g Cd ha^{-1} $year^{-1}$. This amount had been reduced by 35.7% from 3.89 g Cd ha^{-1} $year^{-1}$ in 1996 when the total area of agricultural land was 16.5 million ha (Statistics New Zealand, 1998). The decline of Cd input from fertilisation matches well with the decrease of the Cd accumulation rate in recent reports mentioned in Section 2.5.

2.4.2 Other sources of Cd in soils

Compared to P fertiliser inputs, the contribution of atmospheric deposition, biosolids application and residues from the clearing and burning of native bush prior to the establishment of pasture to the accumulation of soil Cd have been considered minimal (Zanders et al., 1999). Fergusson and Stewart (1992) found that Cd deposition fluxes dropped approximately exponentially from Christchurch city centre. With a 10 - 20 km radius of Christchurch, the amount of Cd deposition from aerosol was equivalent to 1.65 g Cd ha^{-1} $year^{-1}$. Later, Gray et al. (2003a) monitored atmospheric Cd deposition at seven rural sites across both North and South Island, and estimated a national mean rate of atmospheric Cd deposition of 0.20 g ha^{-1} $year^{-1}$, with a range between 0.09 and 0.36 g ha^{-1} $year^{-1}$. The contribution of biosolids application to soil Cd is usually considered negligible (<5% of total), except in exceptional circumstances (Loganathan et al., 2008). Data from Al Mamun et al. (2016) showed that the Cd concentration in biosolids used in NZ was 1.8 mg kg^{-1}, which could introduce a significant amount of Cd into soils if they were applied to soils. The increase of Cd concentration induced by shed effluent application was also reported in dairy soils (Carrick et al., 2014), Mānuka *(Leptospermum scoparium)* soils (V.P. Reis et al., 2016) and reforest degraded soils (Gutierrez-Gines et al., 2017). Apart from the positive effects on soil Cd accumulation, McLaren et al. (2004) reported the application of sewage sludge reduced soil pH and enhanced soil Cd leaching.

2.4.3 Cadmium removal by crops and grazing animals

Cadmium uptake by plants can result in Cd loss from soils. This has been shown in pasture systems (Reiser et al., 2014; Roberts & Longhurst, 2002; Roberts et al., 1994). Rothbaum et al. (1986b) estimated the average annual amount of Cd uptake by grass-clover pasture at 0.4 g ha^{-1}, only consisting of 2% of additional Cd from P fertiliser application. Similar results were obtained by Loganathan et al. (1995), who assessed that pasture induced 0.55 to 1.14 g Cd uptake from soil, accounting for 1.5 - 4.5% of fertiliser Cd in a 10-year SSP fertiliser trial near Palmerston North. Reiser et al. (2014) revealed that Cd concentrations in 90% of herbage samples from 69 pastoral sites were < 0.2 mg kg^{-1}, with a mean value of 0.13 mg kg^{-1}. Based on this herbage Cd concentration, assuming annual pasture dry matter yield of 10 t ha^{-1}, the average amount of Cd uptake in a ryegrass/clover pasture can be estimated at 1.3 g ha^{-1} $year^{-1}$. This coincides with a recent study conducted in ryegrass/clover mixed pasture with similar soil Cd concentration (0.20 mg kg^{-1}) finding that Cd uptake by plants was considered at 1.2 g ha^{-1} (Gray et al., 2017c). However, many studies in NZ showed that Cd concentrations in muscle or milk products were very low (Bramley, 1990; Lee et al., 1996; Roberts et al., 1994). All Cd accumulated in the fleece-free body only represented for around

0.35 - 0.50 % of daily Cd intake while the majority was returned to the soil through faeces (Lee et al., 1996). The Cd lost from pasture soils via animal grazing can be ignored (Sheppard et al., 2009).

In cropping systems, plant uptake of Cd can account for a considerable proportion of total Cd loss from soils. These losses are determined by the yield of the harvested crop and its relevant Cd concentrations. This is a major difference of Cd movement from pasture systems where the Cd accumulated in plants may return to soils though faeces deposited by animals. In European agricultural soils, Six and Smolders (2014) estimated average Cd lost via off-take at 0.20 ha^{-1} yr^{-1}, consisting of around 8 % of total Cd loss. In NZ, there is currently no Cd off-take losses data in cropping lands. However, to some extent, it can be calculated based on empirical data. For example, in a field-trial study, Cavanagh et al. (2016) reported a mean value of potato Cd concentration of 0.025 mg kg^{-1} (fresh weight) with a soil Cd concentration at 0.80 mg kg^{-1} in Waikato. Assuming a potato farm set up in Waikato arable farms (median soil Cd concentration, 0.64 mg kg^{-1}) (Cavanagh, 2014) with an annual yield of 42 t ha^{-1} (Ministry for Primary Industries, 2009), up to 0.86 g Cd can be removed at harvesting, which would account for 6.5% of fertiliser Cd (assuming an inputs of 72 kg P ha^{-1} with 184 mg Cd kg^{-1} P) if the potato Cd concentration changes proportionally with the soil Cd concentration. With regard to wheat, previous studies have shown that wheat grains can accumulate Cd concentrations to between 0.03 and 0.11 mg kg^{-1} with a mean value of 0.054 mg kg^{-1} (FW) (Gray et al., 2001; Gray et al., 1999a; Gray et al., 2002). The estimated amount of Cd removal is ca. 0.65 g ha^{-1} $year^{-1}$, assuming a typical annual yield of 12 t ha^{-1} (FAR Cultivar Evaluation, 2017). The annual estimated amounts of Cd removal via crops are higher than those reported in the European countries, 0.44 g Cd ha^{-1} for potato and 0.2 g Cd ha^{-1} for cereal (Six & Smolders, 2014). In their study, the yield of potato was estimated at only 25.9 t ha^{-1} and cereal at 5.1 t ha^{-1}. These off-take amounts are lower than those in rice which ranges from 5 to 55 g ha^{-1} $year^{-1}$ (Zhao et al., 2015).

2.4.4 Cadmium loss from soils via leaching and surface runoff

Williams and David (1976) estimated that approximately 50% of the Cd derived from 20 years of P fertiliser usage was lost due to leaching from Australian cropping soils. In NZ, Loganathan and Hedley (1997) estimated that Cd loss from the top 20 cm soil through leaching was negligible, representing < 5% of applied Cd. Gray et al. (2003b) also confirmed that annual Cd losses through leaching were 0.27 – 0.86 g ha^{-1}, representing 5 – 15% of annual additional Cd from P application and 0.07 – 0.23% of the total soil Cd within 0 – 25 cm depth. They suggested that the pH of the leachate and drainage volume were the determining factors, but they did not observe significant relationships between the amounts of Cd leached and soil properties (e.g. soil total C and total Cd). A subsequent study by McDowell (2012) found that 56 years application of superphosphate (24 kg P ha^{-1}) at the Winchmore

dryland field trial raised Cd concentrations of the top 7.5 cm soils from 0.08 to 0.32 mg kg^{-1} (i.e. an accumulation rate of 4.3 µg Cd kg^{-1} $year^{-1}$); however an irrigation trial (*ca*.770 mm $year^{-1}$) run in parallel showed only an increase to 0.24 mg kg^{-1} with a yearly enrichment rate of 2.9 µg Cd kg^{-1} $year^{-1}$. He estimated that irrigation causes 1.4 to 2.8 g Cd to be lost from this soil horizon annually. In an indoor leaching experiment conducted with Canterbury stony soils (NZ *Recent Soil*; depth: 70 cm, soil Cd: 0.35 mg kg^{-1}), Carrick et al. (2014) investigated the effect of dairy shed effluent application on Cd leaching and found that when 150 mm drainage was induced, around 0.25 - 0.32 g ha^{-1} Cd was lost through leaching, which accounted for 37- 42% of the additional Cd via the effluent application. Similarly, on a stony winter dairy-grazed farm (soil depth: 15 cm, soil Cd: 0.26 mg kg^{-1}) in Southland, average Cd leaching loss was estimated at 0.30 g ha^{-1} $year^{-1}$ (Gray et al., 2017b). As well as leaching loss, Cd loads in surface outwash were estimated to range between 0.17 - 0.92 Cd kg^{-1} $year^{-1}$ in flood irrigation trials carried out in the Winchmore field trial sites (McDowell, 2010). However, the results from a similar trial in Otago showed that Cd loss in surface flow was only 0.06 g ha^{-1} $year^{-1}$ for forage crop pasture and 0.04 g ha^{-1} $year^{-1}$ for grass pasture (Gray et al., 2017c). Combining the effects of both leaching and overland outwash, Salmanzadeh et al. (2017b) assessed that irrigation caused average annual losses at 2.3 g Cd ha^{-1} from the top 10 cm and 7.2 g Cd ha^{-1} from the top 40 cm of the soil profile compared to unirrigated soils in NZ dairy systems. In particular, in a Canterbury dairy farm (NZ *Pallic Soil*), they found irrigation induced up to 11 g of Cd removed from top 10 cm soil horizon annually.

2.5 Rate of cadmium accumulation in agricultural soils

The low solubility of Cd in NZ soils helps to explain the relatively low Cd removal rates via leaching or plant uptake and favours accumulation (Table 2.2). Gray and McDowell (2016) reported that the annual Cd lost via leaching in organic soils varied between 0.14 and 0.21 g ha^{-1}, lower than that in Pumice (0.35 g ha^{-1}), Allophanic (0.86 g ha^{-1}), Brown (0.54 g ha^{-1}), Pallic (0.27 g ha^{-1}), and Recent (0.5 – 0.8 g ha^{-1}) soils (Carrick et al., 2014; Gray et al., 2003b).

Evidence for Cd accumulation in NZ soils has been gathered from a combination on long-term field trials, as well as surveys at the wider regional level. Loganathan et al. (1995) investigated soil Cd accumulation on a grazed hill pasture trial near the city of Palmerston North, which had been fertilised with superphosphate for over 20 years. They found that with an average annual superphosphate input of ca. 38 kg P ha^{-1} $year^{-1}$, the Cd concentrations increased at the rates of 11.3 and 17.8 g ha^{-1} $year^{-1}$ on steep and shallow slopes respectively. In the South Island, Gray et al. (1999b) estimated an accumulation rate of 7.8 g Cd ha^{-1} $year^{-1}$ over a similar period of time at a long-term fertiliser trial at Winchmore, Canterbury, which had had superphosphate applications of 34 kg P ha^{-1}

year^{-1}. Kim (2005) estimated the average Cd accumulation rates for different land uses between 1939 and 2003 in the Waikato region and found similar accumulation rates for horticultural (8.1 µg kg^{-1} year^{-1}) and pastoral (9.0 µg kg^{-1} year^{-1}) soils, while the accumulation rates in intensive farming systems with soils used for growing potatoes and dairying were higher showing accumulation rates of 22.3 and 14.5 µg kg^{-1} year^{-1} respectively. He also estimated the length of time it would take before soil Cd concentrations would exceed the 1 mg kg^{-1} maximum guideline value recommended by the New Zealand Water and Wastes Association (NZWWA, 2003) and predicted that it could occur in the short-term in dairy systems (16 years), followed by horticultural (30 years) and drystock (40 years) farming systems (Kim, 2005). Loganathan et al. (2008) looked at Cd concentrations in pastoral soils at a national scale and estimated an average accumulation rate of 8.40 g ha^{-1} year^{-1}, which suggested that the soil Cd concentrations could double within 36 years. The compilation of survey results suggest that median Cd concentrations of dairy and cropping soils increased significantly between two time periods while those of orchard and non-agricultural soils experienced a decline (Figure 2.3A). All five types of agricultural soil showed significant increases of Cd concentrations (Figure 2.3B). Briefly, compared with soil Cd concentration analysed from 2006 to 2007, Volcanic soil had the largest percentage of increase of Cd concentrations (40.9%) from 2008 to 2014, followed by Pumice soil (40%) and Organic soil (20.5%), while Sedimentary soil exhibited the lowest (10%). The increase of Cd concentration in soils used for dairy farming was confirmed by Stafford et al. (2018c), which compared Cd concentrations in dairy blocks with different management history. They found that blocks with longer duration of P application had higher Cd concentrations. Kelliher et al. (2017) also observed a continuous accumulation of soil Cd at the Winchmore fertiliser trial.

When comparing with published Cd loss rates from NZ soils, the higher input rates generally suggest that there could be a net accumulation of Cd in NZ soils (Table 2.4). However, the high Cd input in previous studies were calculated from the high Cd concentrations in fertiliser, such as 480 mg Cd kg^{-1} P (Rothbaum et al., 1986b), 336 – 399 mg Cd kg^{-1} P (Loganathan et al., 1995) and 280 mg Cd kg^{-1} P (Kim, 2005). The Cd concentration in the current fertiliser (184 mg Cd kg^{-1} P) is much lower (Taylor et al., 2017). Therefore, in the last 10 years some studies have suggested that the Cd accumulation rate in some NZ soils was decreasing, with contrasting evidence of net increases of Cd from soils. Measurements of historic soil samples from a long-term pasture trial located at Whatawhata in the Waikato region found that under low rates of P fertiliser use (< 50 P kg ha^{-1} year^{-1}) and current Cd concentrations in phosphate fertiliser (180 mg Cd kg^{-1} P), soil Cd concentrations are unlikely to reach the 1 mg kg^{-1} guideline (Figure 2.5A) (Schipper et al., 2011). At another long-term trial at Winchmore in Canterbury, looking at flood-irrigated pastures, both McDowell (2012) and Salmanzadeh et al. (2017a) suggested soil Cd was unlikely to accumulate further if the rates of P fertiliser usage (24 P kg

ha^{-1} $year^{-1}$) and Cd content in P fertiliser were maintained at their contemporary levels (Figure 2.5B). McDowell (2012) showed that there may have been a net loss of Cd from soils at the Winchmore irrigation trial since 2003, due to higher production (resulting in more offtakes of Cd) and higher leaching of Cd on irrigated land. Although the slowdown of the Cd accumulation rate is also suggested by recent monitoring reports (Abraham et al., 2016; Cavanagh, 2014; Taylor et al., 2017), there is not adequate evidence supporting the conclusion that average soil Cd concentrations in various regions and soil types have reached a plateau. There are three reasons limiting its generalisation in NZ agricultural systems. First, at the Winchmore sheep farming trials, annual P application rates were lower than those in other farming systems. Butler and Johnston (1997) investigated the annual P usage in Waikato and Bay of Plenty, and found that P fertiliser application was 24 kg ha^{-1} $year^{-1}$ in drystock systems, much lower than dairy (56 kg ha^{-1} $year^{-1}$) and vegetable (147 kg ha^{-1} $year^{-1}$) farming systems. Secondly, the Winchmore trials were dominated by Sedimentary (Brown) soils with relatively lower soil pH (5.2 – 5.5) (McDowell, 2010) in comparison to the Waikato region with a median soil pH of 6.4 for cropping farms and 6.1 for dairy pasture (Taylor, 2013). According to the results from a Cd leaching experiment (Gray et al., 2003b), higher soil pH contributes to less Cd loss via leaching, implying that Waikato soils may have a smaller leaching rate of Cd with the same volume of total drainage. Thirdly, the Winchmore trials were flood irrigated. According to Moog (2009), spray irrigation represents for 74% of irrigated pastures in NZ. In flood-irrigation lands, average 25% of irrigation was estimated to loss via surface runoff (McDowell & Rowley, 2008), which contributed to a significant amount of Cd loss in outwash (0.17 – 0.92 g Cd ha^{-1} $year^{-1}$) (McDowell, 2010).

Table 2.4 Summary of studies looking at specific Cd inputs and losses into NZ pasture soils.

Cd mass balance		Cd input/loss (g ha^{-1} $year^{-1}$)	Soil order	Reference
Cd inputs	Phosphate fertilisers	19.2 *	NS	(Rothbaum et al., 1986b)
		11.3 – 17.8 *	*Brown*/*Granular*	(Loganathan et al., 1995)
		3.0 – 7.8 *	*Brown*	(Gray et al., 1999b)
		8.4 – 21.6 *	NS	(Kim, 2005)
	Atmospheric deposition	1.65	NS	(Fergusson & Stewart, 1992)
		0.09 – 0.36 *	NS	(Gray et al., 2003a)
	Bio-solid	NS		
Cd losses	Pasture uptake	0.40	NS	(Rothbaum et al., 1986a)
		0.55 – 1.14 *	*Brown*/*Granular*	(Loganathan et al., 1995)
		1.20	*Pallic*	(Gray et al., 2017c)
	Leaching	0.27 – 0.86 *	*Pumice*/*Allophanic*/ *Brown*/*Pallic*	(Gray et al., 2003b)
		1.40 – 2.80 *	*Brown*	(McDowell, 2012)
		0.25 – 0.32	*Recent*	(Carrick et al., 2014)
		0.15 – 0.39	*Organic*	(Gray & McDowell, 2016)
		0.30	*Recent*	(Gray et al., 2017b)
		2.3 – 7.2 *	*Pumice*/*Gley*/*Recent*/ *Brown*/*Pallic*	(Salmanzadeh et al., 2017b)
	Outwash	0.04 – 0.92	*Brown*	(McDowell, 2010)
		0.06 – 0.04	*Pallic*	(Gray et al., 2017c)

NOTE: most studies were carried out over a year and those marked with * were over 2 years; NS means no available information.

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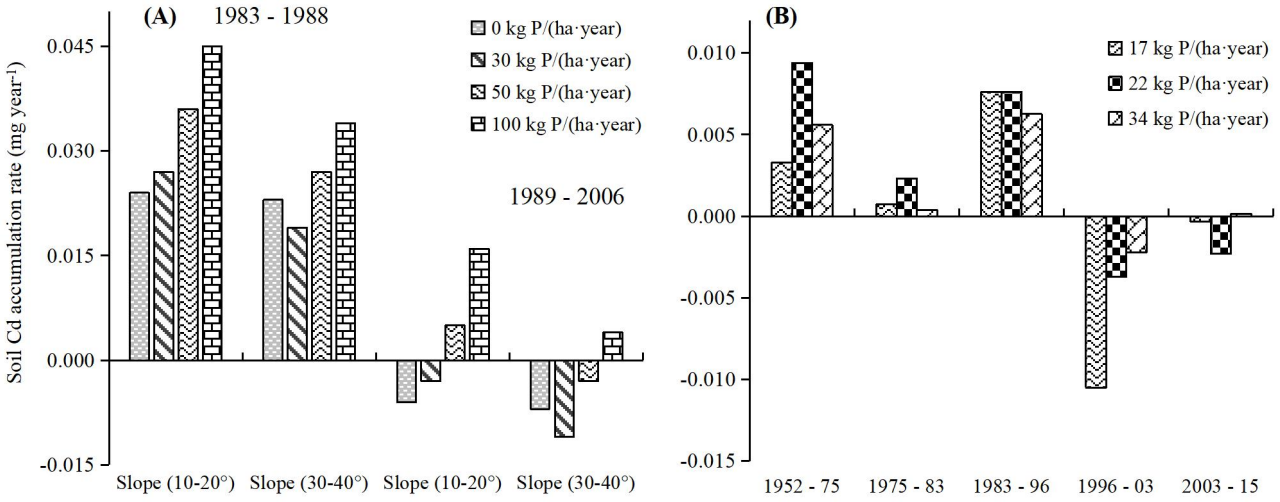

Figure 2.5 The annual Cd accumulation rate in two field research stations at (A) Whatawhata and (B) Winchmore. Soil Cd concentrations in the Whatawhata trial were from (Schipper et al., 2011) and data in the Winchmore trials were summarised from previous monitoring results (Gray et al., 1999b; McDowell, 2012; Salmanzadeh et al., 2017a). Cd data between 2004, 2007 and 2009 from McDowell (2012) were excluded due to possible analytical error.

2.6 Managing the potential risk posed by high soil Cd concentrations in NZ

In response to increasing concerns of accumulation of Cd in agricultural soils, the fertiliser industry in NZ developed the Tiered Fertiliser Management System (TFMS) which was adopted subsequently by the Cadmium Working Group. The TFMS is composed of four tiers with a target to maintain soil Cd concentrations within acceptable ranges over the next 100 years (Sneath, 2015). The TFMS suggests that farmers sample their soils at five-year intervals following standard soil Cd sampling protocols (MAF, 2011). If the soil Cd concentration is > 0.6 mg kg^{-1}, appropriate management options are allocated to one of four 'Tiers' to minimise Cd accumulation rates by progressively restricting the types of P fertilisers and their application rates to prevent accumulation of Cd reaching over 1.8 mg kg^{-1} within 100 years (Appendix Table A2).

Apart from the introduction of fertiliser Cd management strategies to reduce the input of Cd to agricultural soils, other NZ studies have assessed the efficacy of different soil amendments to minimise Cd accumulation in plants (Al Mamun et al., 2016; Al Mamun et al., 2017; Bolan et al., 2003b; Salmanzadeh et al., 2016; Valentinuzzi et al., 2015). The soil amendments that have been tested in NZ are lime (Bolan et al., 2003b; Valentinuzzi et al., 2015), phosphate (KH_2PO_4) (Bolan et al., 2003a), biosolids (Black et al., 2012b), lignite (Al Mamun et al., 2016; Simmler et al., 2013), and compost (Al Mamun et al., 2016; Al Mamun et al., 2017). These amendments reduce soil Cd

bioavailability by inducing alteration of soil pH or increasing cation binding sites, which influences Cd hydroxyl speciation in soil solution, or increasing Cd sorption by soil particles. Using a sequential extraction procedure to fractionate soil Cd, Bolan et al. (2003b) found that the lime addition reduced the concentrations of Cd in soluble and exchangeable forms while less available forms (inorganic-bound Cd) of Cd fractions in soil were increased. Similar reductions of soil weak salt solutions extracted Cd concentration induced by the lime application were also reported in other studies (Al Mamun et al., 2017; Benyas et al., 2018; Bolan et al., 2003b; Gray et al., 1999c; Valentinuzzi et al., 2015). However, similar to international studies (Smolders, 2001), the effects of lime addition on Cd accumulation/uptake in plants vary between studies. Gray et al. (1999c) found that significant liming-induced decline of Cd concentrations in lettuce, clover, carrot and ryegrass. Valentinuzzi et al. (2015) also reported that liming lowered Cd accumulated by pasture forage lupin. On the contrary, Bolan et al. (2003b) and Benyas et al. (2018) observed an increase in plant Cd concentration after lime application, likely due to the lime-borne Ca^{2+} at high pHs or lime-induced Zn deficiency. Inconsistent effects of amendments on plant Cd concentrations also occur in C-rich materials which are another typical amendments for Cd chemical immobilisation in NZ. Simmler et al. (2013) found that the application of 1 % (dry matter) lignite to pasture soil could decrease 30% of Cd uptake by perennial ryegrass. Al Mamun et al. (2016) and Al Mamun et al. (2017) showed that Cd uptake by vegetables (onion, lettuce, spinach, and potato) was lower in composted amended soils. However, the results from McLaren et al. (2004) showed an increase of Cd leaching after the application of sewage sludge. Conflicting results on the effects of amendments on plant Cd concentrations may be due to the differences of types and rates of application of amendments (Al Mamun et al., 2016; Al Mamun et al., 2017), soils properties (Al Mamun et al., 2016) and targeted plant species (Benyas et al., 2018; Gray et al., 1999c). The discrepancy of plant Cd concentrations in response to amendment application between studies highlights various specific mechanisms, such as the Ca^{2+} from lime competing for adsorption sites with Cd (Bolan et al., 2003b), the amendment-induced Zn deficiency (Benyas et al., 2018) and the introduction of Cd from the amendments (McLaren et al., 2004), that influence Cd accumulation in plants.

2.7 Conclusion

In New Zealand agricultural systems, the historic applications of Cd-rich P fertiliser has elevated the soil Cd concentration in some soils. The geo-accumulation index states that soil Cd contamination are generally at *low* to *medium* levels in NZ. Of the different NZ Soil types, the highest median Cd concentrations are found in Volcanic soils, while soils used for dairy farming have the highest median soil Cd concentration among the different land uses. With the reduction of Cd concentration in P

fertiliser, it has been argued whether the accumulation of soil Cd has reached a plateau on a national level, as the soil Cd accumulation rate has slowed down or even declined in some agricultural soils. However, trends toward accumulation of soil Cd are apparently observed in intensively farmed areas, especially in regions dominated by Volcanic and Organic soils, where Cd_{plant}/Cd_{soil} and $Cd_{soluion}/Cd_{soil}$ ratios are lowest (Table 2.2) due to strong Cd adsorption to soil. The combination of high P application rates and low rates of Cd loss results in Cd accumulation in these soils. The variable distribution in soil Cd concentration between regions highlights the effects of P fertiliser usage (including the duration of P use, application rate and Cd concentration in fertiliser) and soil types on soil Cd accumulation. However, there is insufficient data to quantify the effects of environmental factors on soil Cd accumulation, which limits a thorough analysis of trends in soil Cd concentrations in whole NZ agricultural soils. Further studies of Cd accumulation are required to establish more long-term soil monitoring trials with various soil orders.

To date, many strategies in NZ have been proposed with the aim to reduce Cd accumulation in plants. The most commonly tested soil remediation method is chemical immobilisation with the application of lime and/or C-rich biowaste. However, the effects of these amendments vary between studies due to the differences in the types and rates of applied materials, soil variables and plant species. Moreover, the effectiveness of most these soil amendments was only evaluated under greenhouse conditions rather than in the field. Further research is required: 1) to understand the specific details of environmental variables in influencing Cd uptake by plants, which may improve the accuracy of soil Cd remediation in safe agricultural products; 2) to investigate soil Cd remediation via chemical immobilisation in field circumstances, which may provide guarantee of the application of these amendments for safe agricultural production.

Chapter 3

Evaluation of different methods for the assessment of cadmium bioavailability in cropping soils under field conditions

A manuscript from this chapter has been prepared to submit into *Science of the Total Environment*.

My contribution to this article: I carried out most of the laboratory work on soil and plant samples . I also collated the data, carried out the data analysis and developed the original draft of the manuscript.

3.1 Introduction

Soil cadmium is the main source of the metal found in tissues of crop plants. However, only a small proportion of Cd in the soil environment is generally available for uptake by plants (bioavailable) and is mainly composed of the readily soluble fractions in the soil (Menzies et al., 2007). An accurate measure of these bioavailable fractions may provide insight into the potential accumulation of Cd in plants, and could thus enable assessment of the toxicity of soil Cd and the risks it may pose to food safety. The factors influencing soil Cd uptake by crop plants can be broadly divided into chemical factors that affect the solubility of Cd in soil and factors that influence the plants' affinity for accumulating the metal in the edible parts. The former have been studied extensively and are reviewed in Chapter 2. Generally, soil pH, soil organic carbon and soil total Cd (Gray and Mclaren (2006), complexing inorganic ligands (such as Cl^-) (Dahlin et al., 2016; Rasa et al., 2006) and metal oxides (Michálková et al., 2014) are thought to be important on account of their influence on the solubility of soil Cd. On the other hand, important plant nutrients whose abundance (or lack of) can affect a plant's affinity to take up Cd. Climactic variables and differences between plants can also play an important role (Reiser et al., 2014). Due to their chemical similarity, Zn concentration in soils may be an important factor influencing Cd uptake by plants (McLaughlin et al., 2011). Both synergistic and antagonistic effects of Zn on Cd concentration in plants have been well documented (Hart et al., 2005; Nan et al., 2002a; Qaswar et al., 2017; Sarwar et al., 2015; Wu et al., 2002). These interactions varied with plant species and cultivar (McLaughlin et al., 2011), plant nutrient status (Robinson et al., 2009), and soil Cd/Zn ratio (Yang et al., 2017). In NZ, Cd and Zn in agricultural systems share a common source which is the application of P fertilisers (Reiser et al., 2014). Reiser et al. (2014) showed that, in addition to soil variables, environmental factors, such as total solar

radiation were significant explanatory variables for the variation of the Cd concentration in pastures. Moreover, Cd concentrations in plant tissue have also been linked to plant-specific effects, such as plant species, varieties and cultivars (Ashrafzadeh et al., 2017; Cavanagh et al., 2016; Gray & McLaren, 2005; Gray et al., 2001; Khan et al., 2010; McLaughlin et al., 2011). Therefore, the challenge for any test of potential bioavailability is to be able to integrate as many of these effects as possible.

A wide-range of methods for assessing bioavailability have been proposed, such as water extraction (Gray & Mclaren, 2006), weak and neutral salts extraction (Gray et al., 2001; Gray et al., 1999d; Guiwei et al., 2010), chelating agents (Jiang et al., 2003; Song et al., 2015), diffuse gradient in thin films (DGT) (Black et al., 2011; Williams et al., 2012) and modelled free ion activity (Black et al., 2012b). Among methods using extractants, Menzies et al. (2007) found weak and neutral salt extraction had the best correlation between soil extractable Cd and Cd concentrations in plant tissue, while the complexing agents (DTPA, EDTA) may overestimate bioavailable Cd in soils containing high amounts of organic carbon. The data obtained from Williams et al. (2012) demonstrated that the DGT technique provided a better prediction of Cd accumulation in rice grain than water extraction under both laboratory and field conditions. Similar results were reported by Black et al. (2011) indicating that DGT was the best method to estimate Cd uptake by wheat and ryegrass. However, Dočekalová et al. (2015) reported low *R*-values (the ratio of DGT measured metal and metal concentration in soil solution) for non-spiked soils. In a pot trial experiment investigating the effectiveness of soil solution, the DGT technique, DTPA extraction and soil total Cd concentration on soil Cd phytoavailability, Soriano-Disla et al. (2010) found none of these methods provided a good estimation of Cd concentration in wheat grain. Poor relationships between the bioavailable Cd measured as the total Cd concentration in soil, EDTA extraction, $Ca(NO_3)_2$ extraction, soil solution and DGT, as well as modelled Cd^{2+} activity and its concentration in wheat shoots and roots were also observed by Black et al. (2014). The applicability of these methods for predicting Cd uptake by plants were soil properties dependent (Song et al., 2015) and plant species dependent (Almås et al., 2006). Although numerous studies have been conducted on the estimation of the bioavailability of soil Cd, no standardised method has been adopted.

Most assessments on the efficacy of these methods to predict Cd concentrations in plants have been undertaken in pots trials under controlled conditions, rather than in the field. Soils in field trials generally are likely to have higher spatial variability of soil moisture and larger heterogeneity of nutrients distribution (Friesl et al., 2006), while the plants grown in the field have lower root densities and a larger range of rooting depths than seen in pot trials. The difference of

environmental variables between greenhouse and natural field circumstances may affect the accuracy of these methods in predicting soil bioavailable Cd (Song et al., 2015). Reiser et al. (2014) investigated the relationships between soil Cd and plant Cd concentration in the field and found that no single environmental variable could adequately estimate the transfer of Cd from soil to pasture. However, there are a lack of similar studies using bioavailability tests as well as soil pseudo-total Cd concentrations ("total") on the prediction of soil Cd accumulation in cropping plants, particularly under field conditions. The aim of this chapter was to determine the most important factors influencing Cd accumulation in cropping system, including onion, spinach, potato and wheat. The work sought to meet this aim by completing the following objectives: (1) Collect paired soil-plant samples from across different regions of NZ (2) compare different soil analysis methods (Cd in soil, Cd in solution, $Ca(NO_3)_2$ extractable Cd and DGT measured Cd) for predicting soil Cd bioavailability (3) consider the influence of regional differences in climactic variables on Cd uptake by the different crop plant species.

3.2 Methods and materials

Paired soil and plant samples were collected from 103 cropping fields where lettuce, onion, potato, spinach and wheat were grown throughout New Zealand between 2016 and 2017 (Table 3.1). There were three types of lettuce which were loose-leaf (Red Frill and Green Frill), romaine/cos (Green Cos, Red Cos, Baby Cos) and crisphead (Iceberg). The cultivars of spinach were *Jedi, Black Glove* and *Nightfall*. The onion cultivar selected for sampling was *Rhinestone*. Additionally, two wheat cultivars (*Reliance* and *Empress*) and two potato cultivars (*Moonlight* and *Innovator*) were collected. The collected samples were from Canterbury (n= 167), Auckland (n = 60), Waikato (n= 57), and Manawatu-Whanganui (forthwith this will be referred to as, "Mana-Wanga"; n= 41), Hawke's Bay (n= 32), Gisborne (n= 22), Tasman (n= 9) and Southland (n= 4). At each site, three or four plots (1.5 × 1.2 m^2) were selected randomly, from which five cores of soil were sampled (diameter × depth, 2.5 × 15 cm). Plant samples were collected from each plot for the different crops as follows: leaves of five lettuce or 5 spinach plants (bunching spinach) or ~100g of baby spinach leaves, five bulbs of onion, five individual tubers from five potato plants, and 100 heads of wheat seeds (grain) were collected within each plot. More sampling details are summarised in Chapter 6 (lettuce, onion and spinach), Chapter 7 (wheat) and Chapter 8 (potato).

Table 3.1 Total number of samples of different crops.

Crops	No. Locations	No. Plant samples	No. Soil samples
Lettuce	4	39	39
Onion	26	75	75
Potato	25	89	89
Spinach	14	69	69
Wheat	34	122	122
Total	103	396	396

All plant samples were thoroughly washed with deionized water (DI, 18.2 MΩ-cm) and oven-dried at 60 °C to constant weight, crushed and ground (A10 Analytical Grinder, Yellowline by IKA) then stored in air-tight polyethylene containers prior to subsequent analysis. Potato tubers were peeled and the peels were discarded. The core parts of the tubers were used for chemical analysis. Similar methods were applied to onion samples. The soil samples were air dried at 25°C to constant weight, crushed and sieved through a 2 mm plastic sieve and stored in zip-lock polyethylene bags at room temperature prior to chemical analysis.

3.2.1 Plant samples

Following the digestion method described in Juranović Cindrić et al. (2015), the prepared plant samples (0.2 g) were digested with 4 mL HNO_3 (50:50, v/v) and 2 mL H_2O_2 using a microwave digestion system (MARSXPRESS, CEM Corp.). The digests were subsequently diluted with DI water to make up a final volume of 10 mL. The digests were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 720 ES – USA) for Cd and Zn concentrations. The plant Cd concentrations are reported on the basis of dry weight in this study if there is no other indication.

3.2.2 Soil analysis

Site information on soil order was obtained from the NZ national soil database (S-map), using the soil-order classification defined by Hewitt (2010). Soil texture was analysed using the pipette method (Claydon, 1989). Soil pH was determined at a solid/water ratio of 1:2.5 using a Metler Toledo pH meter (Mettler Toledo Seven Easy) (Blakemore & Price, 1987). Total carbon (C) and nitrogen (N) were measured by combustion using an Elementar Vario MAX CN element analyser. Soil extractable chloride (Cl) concentrations were analysed in a 0.45 μm pre-washed membrane filtered 1:5 soil:water extract by ion chromatography (Dionex ICS-2100, Thermo Fisher Scientific Inc.). Bioavailable soil P (Olsen P) was tested by the bicarbonate extraction at a commercial laboratory (*Hill Laboratories Ltd., Hamilton, New Zealand)* (Olsen, 1954). All results are expressed on an oven-dry (105°C) soil basis. The cation exchange capacity (CEC) and base saturation (BS) of soils were

measured using the 1 M neutral ammonium acetate extract method of Blakemore and Price (1987). The pseudo-total soil metals and total P concentrations were analysed using concentrated acid digests (Simmler et al., 2013). Soil (0.5 g) was digested in 3 mL trace element grade concentrated nitric acid (HNO_3, > 65%) and 3 mL hydrogen peroxide (H_2O_2, 30%). The digest was diluted to 25 mL with DI water and filtered with a Whatman 52 filter paper. The soil digests were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for Cd and ICP-OES for other metals and P.

3.2.3 Soil analysis for Cd bioavailability

To address variation in Cd uptake by plants in different regions, a further systematic study was employed to investigate the relationship between soil Cd bioavailability and environmental factors using a subset of samples (forthwith "bioavailability survey") due to budgetary and time-management reasons (Table B3 in Appendix). To keep the cultivar variety consistent, the cultivar of spinach in subsequent analysis was Jedi, onion was Rhinestone, potato was Moonlight and wheat was Reliance. Lettuce was excluded in the analysis, due to the insufficient number of samples of single cultivar.

Calcium nitrate ($Ca(NO_3)_2$) extraction was used to estimate the bioavailable fraction of soil Cd. According to the methodologies described by Gray et al. (1999b), soil $Ca(NO_3)_2$ extraction was analysed by weighing 5 g of soil into a centrifuge tube containing 30 mL with 0.05 M $Ca(NO_3)_2$. Tubes were agitated for 2 h in an end-over-end shaker, centrifuged for 10 min at 3300 rpm, and finally filtered using a Whatman 52 filter paper. Final extracts were analysed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent-7500cx) to determine Cd and Zn concentration.

The application of diffusive gradients in thin-films (DGT) on the bioavailability of metals was modified from the methodology described by (Zhang et al., 1998). Briefly, air dried soil (20 g) was weighed into a small cylindrical container (5.0 $\times$ 1.3 cm). Then, DI water was added to the soil to achieve near 100% maximum water-holding capacity and maintained for 48 h. A standard DGT soil probe (DGT Research Ltd.) was deployed, ensuring thorough contact between the soil slurry and the device sampling window . The deployment took place in a moisture-saturated atmosphere for 24 h, during which the temperature was 21 $\pm$ 1°C. At the end of the deployment the DGT devices were cleaned with DI water and dismantled. The Chelex-100 resin gels were eluted with 1 mL of 1 M HNO_3 for 24 h. Following DGT retrieval the soil slurry was transferred into a 50 mL centrifuge tube and centrifuged at 2000 rpm for 10 min. The supernatant was then filtered through a polyethersulphone (PES) disc filter (0.45 μm) to extract the porewaters. All extracts (porewater) were diluted two-fold

with 0.1 M $Ca(NO_3)_2$. All extracts and eluents were diluted with 2% HNO_3 five-fold before metal analysis using ICP-MS.

The DGT extractable concentrations of Cd ($C_{DGT\text{-}Cd}$, $\mu g\ L^{-1}$) and Zn ($C_{DGT\text{-}Zn}$, $\mu g\ L^{-1}$) were calculated according to Equation (1) ((Zhang et al., 1998)).

$$C_{DGT} = M \times \Delta g / (D \times A \times t) \quad \text{Eq. (1)}$$

Where M is the total mass of Cd or Zn bound by the resin gel (ng gel^{-1}); Δg is the combined thickness of the diffusive hydrogel layer (0.08 cm) and the filter membrane (0.014 cm); D is the temperature-specific diffusion coefficient of Cd or Zn in the diffusive gel ($cm^2 \cdot s^{-1}$); A is the physical exposure area of the DGT device (3.08 cm^2); and t is the deployment time (s). The soil solution concentrations are reported as ug L^{-1}.

3.2.4 Climate information

Weather data for each sampling site was obtained from the nearest climate station of the National Institute of Water and Atmospheric Research. Specifically data on total solar radiation, total annual rainfall, and the average daily air temperature (forthwith 'average temperature') for the growth period were collected. As we did not have the exact dates for planting for the different crops in the different regions, we assumed that the growth period for wheat was eight months, onion was seven months, potato was six months and spinach was two month, based on information provided by the growers.

3.2.5 Quality control

A duplicate test was used in every 20 samples to assess the repeatability of analysis. Several internal and external reference soils (NIST Montana 2711; Interlab internal WEPAL soil 921; Interlab internal WEPAL soil 981), and plants (NIST 1573a, tomato leaves; ASPAC internal clover; ASPAC internal beetroot) were used as standard reference materials to assess the accuracy of the metals analysis (Table BI and B2 in Appendix). The recovery ratios of the certified soils varied from 96 - 106% for Cd, while certified plants ranged between 92 - 96 % for Cd.

3.2.6 Statistical analysis

The analysis was mainly composed of three parts (1) a one-way analysis or Kruskall-Wallis test was conducted to determine whether there were differences in both soil and plant Cd concentrations between crops species at the 5% probability level after assessing for normality; (2) correlations between plant Cd or Zn concentrations and environmental variables were investigated using

Spearman correlation coefficients; (3) stepwise multiple linear regressions were performed to investigate the relationships between plant metals concentrations and environmental variables and the relationships between bioavailable metal concentrations and soil properties. All correlation or multiple regression analysis between variables were log-transformed if non-normally distributed (Shapiro-Wilk's test) before analysis. The variable inflation factor (VIF) was applied to minimize multicollinearity of the variables. The predictors with VIF < 5 were used in the regression models. The stepwise linear regression analysis was carried out using Minitab 17 (Manufacturer, Company HQ), and all other statistical analyses were carried out using the R software (De Mendiburu, 2014).

3.3 Results

3.3.1 Soil cadmium concentrations in different New Zealand regions and soil orders

The surveyed soils varied widely in pH (4.6 – 7.6), clay content (11 – 76%), total carbon content (0.6 – 20.0 %) and concentrations of elements found in major soil minerals (Al, Fe and Mn) (Table 3.2). The Cd concentrations varied from 0.02 to 1.41 mg kg^{-1}, with a median concentration of 0.20 mg kg^{-1} and a mean of 0.28 mg kg^{-1}. 10.1% of sampled soils in this study had Cd concentrations higher than the TFMS tier 1 trigger of 0.6 mg kg^{-1}, and 1.5% higher than the TFMS tier 2 trigger of 1.0 mg kg^{-1}. Spearman correlation analysis indicated the total soil Cd concentration was positively significantly correlated with soil total P concentration, Olsen P concentration, soil clay, total carbon concentration, soil CEC and total soil Al and Mn concentrations. Consistent with previous national soil survey results (Cavanagh, 2014), the median soil Cd concentrations in the regions decreased in the following order: Waikato > Auckland >> Manawatu-Wanganui > Tasman >> Hawkes Bay > Southland > Gisborne >> Canterbury, with significant differences (>>) between many of the regions (Figure 3.1). The median Cd concentration in the Waikato was 0.53 mg kg^{-1}, four-fold higher than that in Canterbury (0.13 mg kg^{-1}) and two-fold higher than that in Manawatu-Wanganui (0.26 mg kg^{-1}). According to the soil-order classification used by Hewitt (2010), Allophanic and Granular soils had the highest median Cd concentrations (0.53 and 0.48 mg kg^{-1}, respectively), followed by Organic soils (0.37 mg kg^{-1}), while the median Cd concentration in Pallic soils was the lowest (0.13 mg kg^{-1}, Figure 3.2). The pattern of soil Cd distribution between soil orders is also similar to results observed by Cavanagh (2014) indicating a relatively higher Cd concentration in Volcanic and Organic soils in comparison to other soil groups by using soil-type classification used by the fertiliser industry (Roberts & Morton, 2009). The soils growing potato had the highest median Cd concentration at 0.33 mg kg^{-1}, followed by spinach (0.28 mg kg^{-1}), onion (0.27 mg kg^{-1}) and lettuce (0.16 mg kg^{-1}) while soils used for growing wheat had the lowest Cd concentration (0.16 mg kg^{-1}) (Figure 3.3A).

Table 3.2 Descriptive statistics of the element content & physicochemical characteristics of analysed soils and Pearson correlation coefficients (log transformation) for each soil parameter with soil total cadmium concentration.

Variable (n = 396)	Min	Max	Mean	Median	Std. Deviation	Skewness	Pearson correlation coefficients	
							Correl.Cd	Correl.Zn
pH	4.56	7.56	6.03	5.94	0.57	0.29	0.13**	0.38**
Sand (%)	1	47	13	10	9.056	1.136	- 0.002	- 0.33**
Silt (%)	19	73	51	51	13.063	-0.381	- 0.57**	- 0.21**
Clay (%)	11	76	31	25	15.04	1.55	0.41**	0.23**
C (g kg^{-1})	6.30	200.20	31.36	25.14	21.28	4.36	0.37**	0.14**
N (g kg^{-1})	0.70	12.50	2.83	2.40	1.53	2.58	0.40**	0.06
P (g kg^{-1})	0.46	5.08	1.53	1.19	0.86	1.45	0.64**	0.73**
S (g kg^{-1})	0.04	1.97	0.45	0.36	0.30	1.98	0.51**	0.44**
Cl (mg kg^{-1})	2.11	160.29	25.10	21.13	19.90	3.28	- 0.16**	- 0.17**
CEC ($cmol_c kg^{-1}$)	6.00	48.00	18.64	17.00	6.44	2.08	0.16**	0.03
Total Base Saturation (%)	38.0	100.0	69.9	67.0	14.99	0.43	0.57**	0.38**
Bulk density (g cm^{-3})	0.45	1.36	0.97	0.99	0.13	-0.94	- 0.56**	- 0.13**
Olsen P (mg kg^{-1})	9.0	351.0	61.4	44.0	51.89	2.14	0.11*	0.25**
Cd (mg kg^{-1})	0.02	1.41	0.28	0.20	0.23	1.81		
Zn (mg kg^{-1})	29.63	253.36	87.00	83.37	25.24	1.09	0.51**	
Al (g kg^{-1})	13.94	142.01	45.57	35.49	29.99	1.62	0.43**	0.72**
Ca (g kg^{-1})	2.02	45.28	7.05	6.81	3.75	3.17	- 0.25**	0.26**
Cr (mg kg^{-1})	<	306.30	22.70	23.57	34.14	4.40	0.01	0.08
Fe (g kg^{-1})	5.89	66.01	24.26	21.51	11.79	1.43	- 0.04	0.63**
K (g kg^{-1})	0.58	11.63	4.02	3.97	2.54	0.77	- 0.74**	0.06
Mg (g kg^{-1})	0.51	40.43	5.04	5.08	3.92	3.87	- 0.62**	0.10*
Mn (g kg^{-1})	0.14	9.32	0.86	0.44	1.20	4.32	0.51**	0.69**
Na (g kg^{-1})	0.12	1.25	0.31	0.24	0.17	2.10	0.27**	0.35**
Ni (mg kg^{-1})	<	359.50	15.80	11.38	29.65	9.25	- 0.04	0.20**
Pb (mg kg^{-1})	2.00	427.53	17.64	14.35	21.87	13.42	0.03	0.40**

* $P < 0.05$, ** $P < 0.01$.

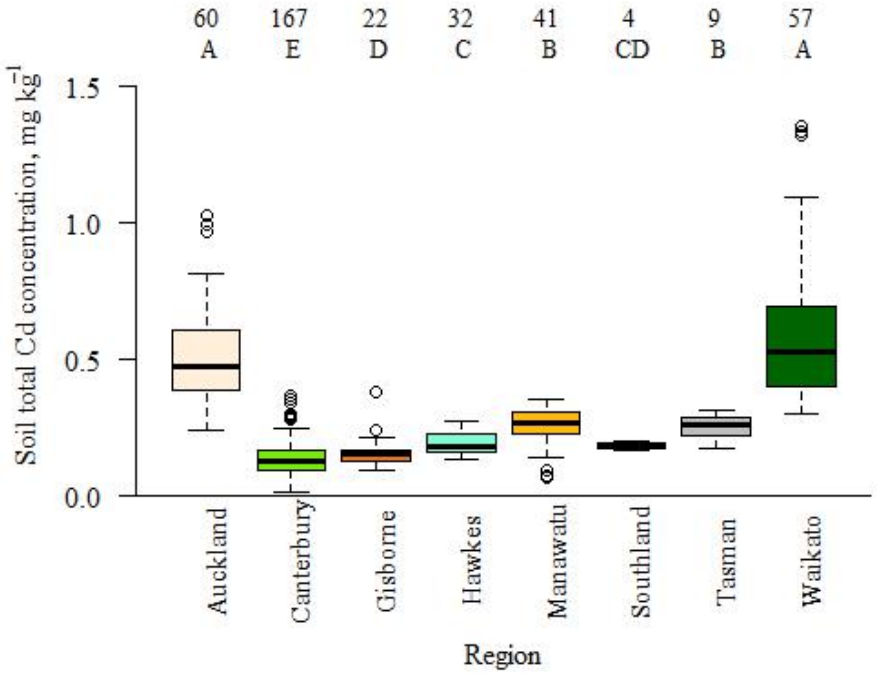

Figure 3.1 Boxplots of Cd concentration in soil according to region showing median, quartile, 90% confidence levels and outliers (filled circles). The numbers above each letter show the sample size of each region. Different letters indicate significant differences between means in the respective categories ($P < 0.05$).

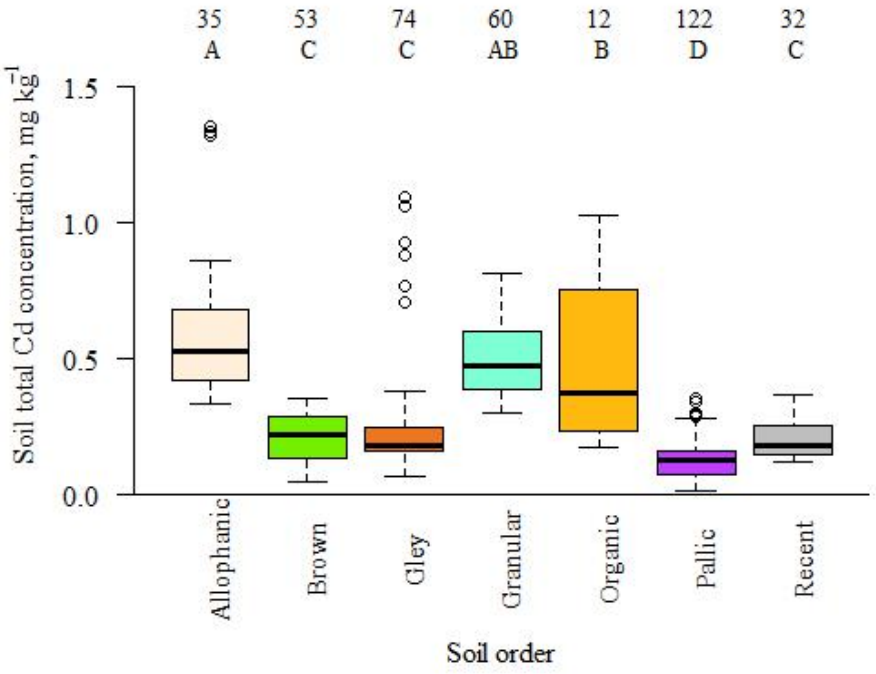

Figure 3.2 Boxplots of Cd concentration in soil according to soil order showing median, quartile, 90% confidence levels and outliers (filled circles). The numbers above each letter show the sample size of each soil order. Data sets with the same letter indicate that their means that are not significantly different from one another ($P > 0.05$).

3.3.2 Cadmium concentrations in plants

The highest median Cd concentration in the edible plant parts was in spinach leaves (0.94 mg kg^{-1}, dry weight, DW), followed by lettuce leaves (0.46 mg kg^{-1}, DW), both of which were significantly higher than the median concentrations in onion bulbs (0.21 mg kg^{-1}) and potato tubers (0.15 mg kg^{-1}) (Figure 3.3B). Wheat grains had the lowest mean Cd concentration (0.07 mg kg^{-1}). In this study, the Cd concentrations in some plant samples exceeded the Australia New Zealand Food Standards, where the maximum limit in leafy vegetables and root & tuber vegetables is both 0.1 mg kg^{-1} (fresh weight, FW). 36.1% of spinach plant samples exceeded this current NZ national food limit if the actual moisture content (91%) was taken into account. In terms of wheat grain, our results indicated 7.8% of collected samples had Cd concentrations exceeding 0.1 mg kg^{-1} (FW). This result is similar to that found by (Gray et al., 2001) who found (10%) of wheat grain samples exceeded the maximum limit. Likewise, Cd in around 3% of potato samples was higher than 0.1 mg kg^{-1} (FW), which is close to the results reported by Kim (2005), who estimated only 1.5% of the potato samples in the Waikato fell above of the safety levels.

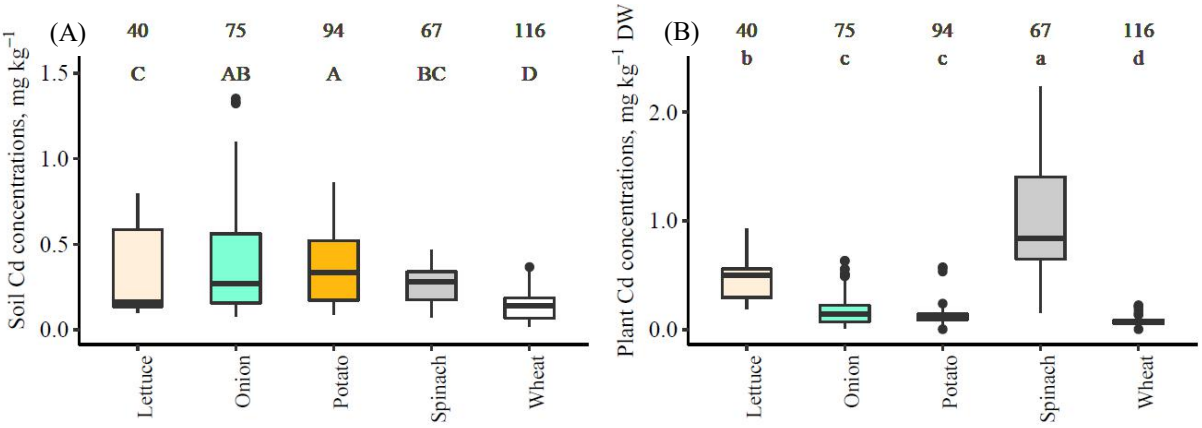

Figure 3.3 Boxplots of Cd concentration in (A) soil and (B) plants (DW) for each crop showing median, quartile, 90% confidence levels and outliers (filled circles). The numbers above each letter show the sample size of each plant. Data sets with the same letter indicate that their means that are not significantly different from one another ($P > 0.05$).

Cd concentrations in crops in the different regions are shown in Table 3.3. The Cd concentrations in lettuce, onion, potato, and spinach varied significantly between regions, while the differences in wheat concentrations were not significant. Lettuce grown in Gisborne had the highest median Cd concentration (0.55 mg kg^{-1}), significantly higher than in Auckland (0.50 mg kg^{-1}), while the median lettuce Cd concentration in Canterbury (0.23 mg kg^{-1}) was the lowest. However, the soil Cd concentration in Gisborne was significantly lower than that in Auckland ($P < 0.05$) (Figure 3.1). In terms of wheat grain, despite of significant differences in soil Cd concentration between regions, there was no significant difference in plant Cd concentration between regions according to the Kruskall-Wallis test. Similarly, the potato Cd concentration between Canterbury and Waikato were similar, while there was more than a 4-fold difference of soil total Cd between these two regions ($P < 0.05$).

Table 3.3 Median cadmium concentrations in five crop species in different regions.

Region	Crop Cd concentration, mg kg^{-1}				
	Lettuce	Onion	Potato	Spinach	Wheat
Auckland	0.503 b	0.314 a	0.132 a	1.128 ab	
Canterbury	0.234 c	0.109 b	0.106 b	0.402 c	0.071 a
Gisborne	0.546 a			0.645 ab	
Hawkes Bay		0.069 c		0.731 bc	0.048 a
Manawatu-Wanganui			0.129 ab	1.394 a	0.064 a
Southland					0.063 a
Tasman				0.802 ab	
Waikato		0.194 a	0.108 b	0.959 ab	

Plant Cd concentrations (dry biomass) with the same letter in same column mean that are not significantly different (P > 0.05) based on Kruskall-Wallis test.

3.3.3 Crop cadmium concentrations in a subset of samples

Consistent with the results shown in Figure 3.3b, the median Cd concentration in the edible parts of a subset of spinach was 0.96 mg kg^{-1} varying between 0.39 and 2.24 mg kg^{-1}, with Cd concentration over five times higher than that in onion bulbs (0.15 mg kg^{-1}) and potato tubers (0.13 mg kg^{-1}), while Cd concentration in wheat grain was the lowest (0.085 mg kg^{-1}) (Figure B1 in Appendix). The physicochemical properties of paired soils and climate information are shown in Table B1 in Appendix. The plant uptake factor (PUF) can be used to assess the plant heavy metal uptake from soil, and is calculated as the ratio of metal concentrations between the plant and soil as: PUF = C_{plant}/C_{soil} (where C_{plant} and C_{soil} represent the plant and soil Cd or Zn concentrations in this study, respectively (Figure 3.4)). The PUF values of Cd for spinach leaves varied from 2.07 to 9.20, with a median value of 4.24, significantly higher than other crops (non-leafy parts) (P < 0.05). At a regional scale, Canterbury had the highest values for PUF of Cd across all crops. Briefly, the median value of PUF for Cd in Canterbury was 1.27 for onion, 0.68 for potato and 4.82 for spinach, which were all significantly higher than those in Waikato (P < 0.05), respectively. Similarly, the median PUF of wheat for Cd for Canterbury soils (0.62) was significantly higher than Hawker's Bay (0.26) (P < 0.05).

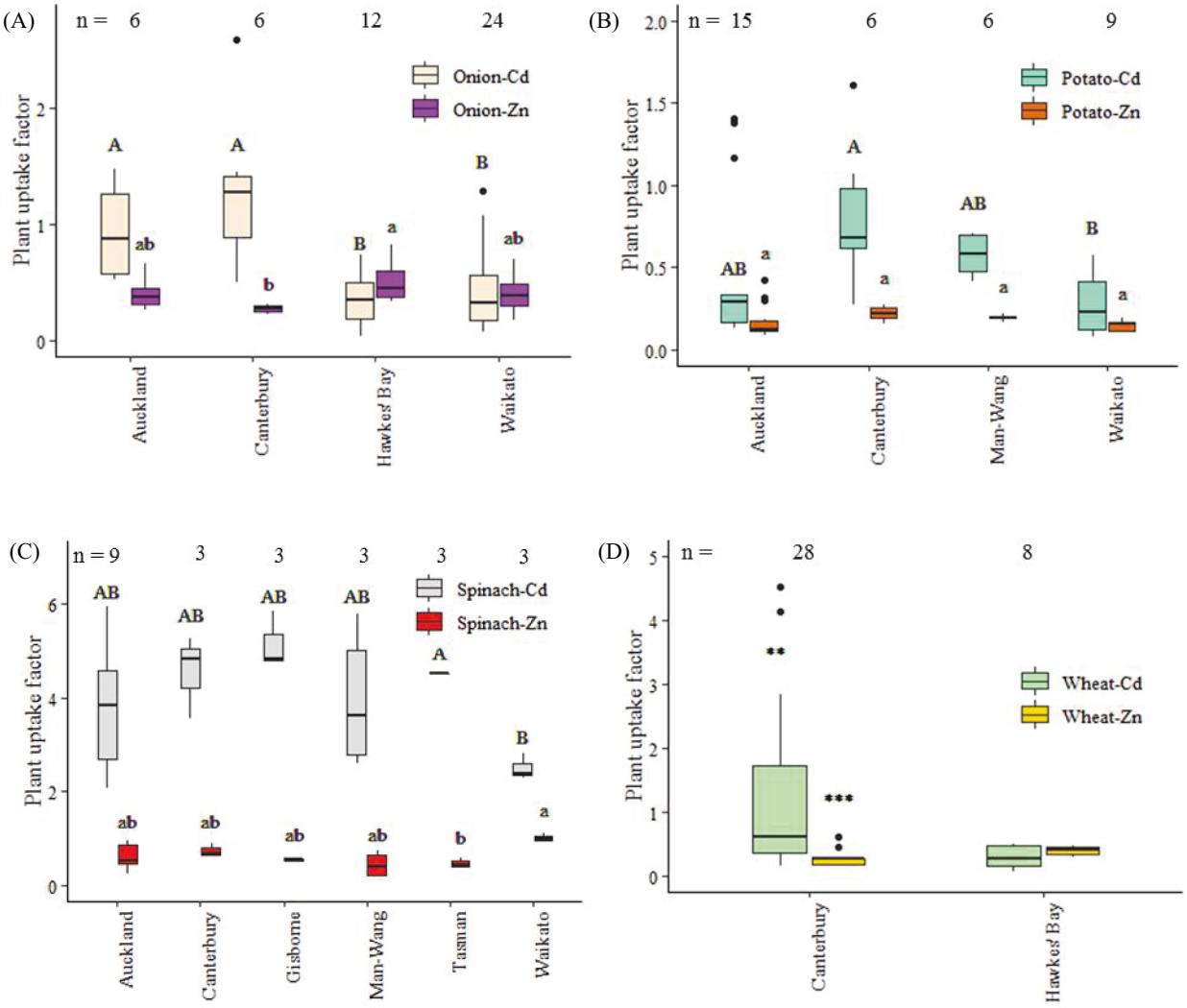

Figure 3.4 Boxplots of the plant uptake factor (PUF) for four crops in different regions showing median, 25th and 75th quartiles, 90% confidence levels and outliers (filled circles). The values PUF with the same letter mean that are not significantly different ($P > 0.05$) after Kruskall- Wallis test for (A) onion and (B) potato samples or after one- way AVONA test for (C) spinach samples. The numbers of asterisks, *** and ** show a significant difference at the $P < 0.001$ and $P < 0.01$, according to a Mann- Whitney test for (D) wheat samples.

3.3.4 Relationship between plant and soil cadmium concentration in a subset of samples

In terms of soil factors, the concentration of Cd in onion was positively correlated to soil Cd concentration, soil Olsen and total P concentration, soil total C, N, S and total Al concentration while negatively correlated to total K, Ca, and Mg concentration and silt content ($P < 0.05$) (Table 3.4). Similarly, 11 out of 22 soil variables exhibited a Spearman correlation coefficient with Cd concentration in spinach leaf at the 0.05 probability level of significance. However, only six soil

variables were significantly correlated with Cd concentration in wheat grain. Likewise, only soil total Cd and P concentration were correlated significantly with potato Cd concentration. For climate factors, there a significant correlation between total rainfall and Cd concentration in onion and spinach. Air temperature was significantly positively correlated with Cd concentration in potato tuber, while it was negatively correlated with wheat grain Cd concentration at the significance level of 0.05.

The relationship between Cd concentration in plants and soil extractants varied between plant species. Soil total Cd concentration was significantly positively correlated with Cd concentration in onion bulb and spinach leaf, but negatively correlated with Cd concentration in potato. The correlation between soil total Cd and wheat grain Cd concentration was not significant. There were significant correlations between $Ca(NO_3)_2$ extractable Cd and Cd concentration in onion (R = 0.48, P < 0.01), potato (R = 0.37, P < 0.05) and spinach Cd (R = 0.81, P < 0.01). DGT measured Cd was only significantly correlated with potato Cd concentration. For wheat, only a significant correlation between grain Cd and porewater Cd concentration was observed. Of the four methods examined, single regression analysis revealed that soil total Cd and $Ca(NO_3)_2$ extractable Cd concentration accounted for 58.9% and 52.9% of the variation of Cd accumulation in spinach (Figure 3.5). The higher coefficient of determination (R^2_{adj}) indicated a stronger relationship between spinach leaf Cd concentration and soil total Cd concentration. Similarly, soil total Cd and $Ca(NO_3)_2$ extractable Cd concentration was significantly correlated with Cd concentration in onion bulb, with the $Ca(NO_3)_2$ extractable concentrations able to explain a greater proportion of the variation in onion Cd concentration (25.9%, Table 3.5). None of the methods tested could successfully predict Cd accumulation in potato tuber at the significance level of < 0.05. In terms of wheat samples, the DGT technique and porewater Cd concentration showed significant differences in the coefficient of determination for grain Cd concentration, but wheat Cd concentration was negatively correlated to Cd concentration measured by DGT.

Table 3.4 Spearman correlation coefficients for Cd & Zn concentrations in plant edible parts and soil and environmental variables.

Parameter	Onion		Potato		Spinach		Wheat	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn
pH	- 0.10	- 0.20	- 0.23	0.05	- 0.60**	- 0.29	0.19	- 0.47**
Sand (%)	0.20	- 0.01	- 0.17	- 0.23	- 0.49*	0.29	- 0.21	0.44**
Silt (%)	- 0.42**	- 0.28	- 0.22	0.15	0.35	- 0.01	0.41*	- 0.72**
Clay (%)	- 0.14	0.40**	0.16	0.19	0.34	- 0.47*	- 0.04	0.42*
Bulk density (g cm^{-1})	- 0.29*	- 0.37*	- 0.28	- 0.77**	- 0.21	- 0.08	- 0.08	0.18
Olsen P (mg kg^{-1})	0.41**	0.17	- 0.14	0.15	0.71**	0.34	- 0.45**	0.27
Total P (g kg^{-1})	0.57**	0.15	- 0.33*	0.09	0.47*	0.56**	- 0.16	0.59**
Total C (%)	0.37**	0.25	0.10	0.47**	0.40*	0.34	- 0.26	0.48**
Total N (%)	0.37**	0.30*	0.11	0.53**	0.28	0.19	- 0.23	0.45**
K (mg kg^{-1})	- 0.32*	0.13	0.07	0.22	- 0.38*	- 0.44*	0.20	- 0.35*
Ca (mg kg^{-1})	- 0.39**	0.27	- 0.20	0.49**	- 0.29	0.02	0.11	- 0.12
Mg (mg kg^{-1})	- 0.47**	0.15	- 0.07	0.07	- 0.27	- 0.44*	0.09	0.05
Na (mg kg^{-1})	- 0.03	0.20	0.08	0.57**	- 0.33	- 0.24	- 0.43**	0.71**
CEC cmol$_c$kg^{-1}	0.17	0.59**	0.07	0.58**	0.21	0.13	- 0.40*	0.65**
C/N ratio	- 0.05	- 0.25**	0.06	0.01	0.01	- 0.02	- 0.20*	- 0.16*
Total Cd (mg kg^{-1})	0.50**	0.09	- 0.34*	- 0.03	0.66**	0.50**	- 0.18	0.43**
Total Zn (mg kg^{-1})	0.12	0.22	- 0.06	0.24	0.20	- 0.03	- 0.17	0.35*
Extractable Cl (mg kg^{-1})	0.09	0.47**	0.25	0.39*	- 0.32	0.02	- 0.11	0.02
Soil Fe (mg kg^{-1})	- 0.27	- 0.04	0.11	0.22	0.49**	0.10	- 0.07	0.28
Soil Al (mg kg^{-1})	0.36*	- 0.10	0.18	0.21	0.55**	0.18	- 0.15	0.48**
Soil Mn (mg kg^{-1})	0.21	0.06	- 0.32	- 0.16	0.46*	- 0.17	- 0.39*	0.66**
Soil S (mg kg^{-1})	0.41**	0.23	0.23	0.80**	0.54**	0.36	- 0.22	0.52**
Total rainfall (mm)	0.50**	0.18	- 0.08	- 0.03	0.66**	0.17	- 0.03	0.15
Air temperature (°C)	0.30*	0.15	0.41*	0.72**	- 0.11	- 0.71**	- 0.51**	0.58**
Total radiation (KMJ M^{-2})	- 0.11	0.49**	0.13	- 0.07	0.01	0.46*	- 0.31	0.29
Plant Cd (mg kg^{-1})		0.01		0.38*		0.45*		- 0.59**
$Ca(NO_3)_2$ - Cd (µg kg^{-1})	0.48**	0.02	0.37*	0.03	0.81**	0.47*	0.02	0.27
$^{Cd}C_{DGT}$ (µg L^{-1})	0.09	0.07	0.36*	- 0.04	- 0.16	- 0.04	- 0.43*	0.35*
^{Cd} Pore water (µg L^{-1})	0.27	0.02	- 0.06	- 0.28	- 0.26	0.06	0.44**	- 0.35*
$Ca(NO_3)_2$ - Zn (µg kg^{-1})	0.04	0.36*	0.11	0.12	0.51**	0.41*	- 0.65**	0.59**
$^{Zn}C_{DGT}$ (µg L^{-1})	- 0.02	0.57**	0.22	0.17	0.08	0.29	- 0.24	0.46**
^{Zn} Pore water (µg L^{-1})	0.23	0.12	0.01	0.09	- 0.47*	- 0.07	0.04	- 0.02

* $P < 0.05$, ** $P < 0.01$.

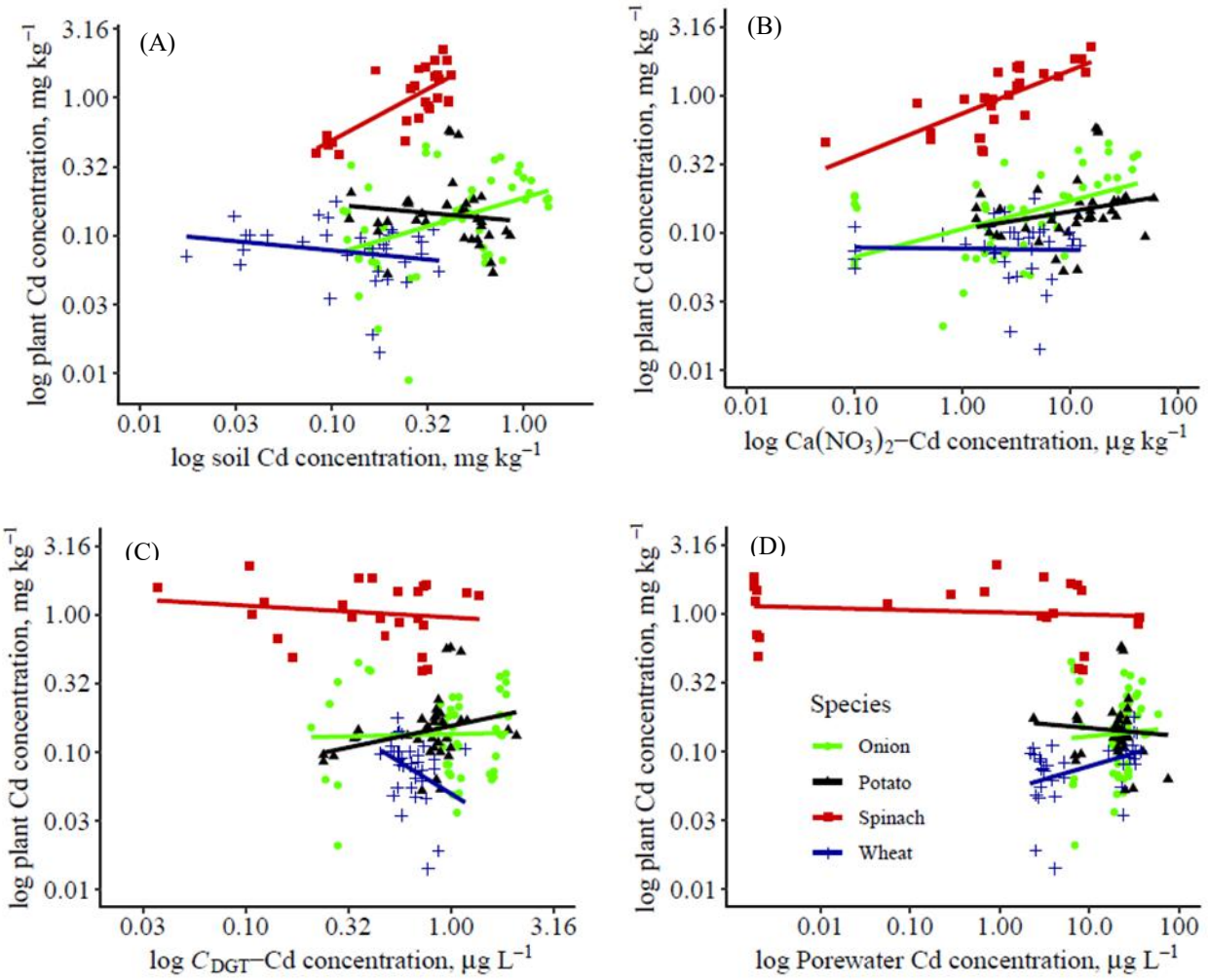

Figure 3.5 Correlations between plant Cd and measured soil Cd, (A) soil total Cd concentration, (B) $Ca(NO_3)_2$ extractable Cd, (C) DGT extractable Cd and (D) soil Cd concentration in soil solution.

Table 3.5 The coefficient of determination (R^2) between Cd concentrations in plants and measured by different methods, i.e., soil total Cd, $Ca(NO_3)_2$ extractable Cd, DGT extractable Cd and soil Cd concentration in soil solution.

Plant	Test	R^2	Plant	Test	R^2
Onion	Total	0.164**	Spinach	Total	0.589***
	$Ca(NO_3)_2$	0.259**		$Ca(NO_3)_2$	0.529***
	DGT	0.001(NS)		DGT	0.023 (NS)
	Porewater	0.001(NS)		Pore-water	0.015 (NS)
Potato	Total	0.013 (NS)	Wheat	Total	0.041(NS)
	$Ca(NO_3)_2$	0.062 (NS)		$Ca(NO_3)_2$	0.001(NS)
	DGT	0.082 (NS)		DGT	0.116*
	Porewater	0.001 (NS)		Pore-water	0.172*

NS = no significant difference, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

Incorporating all extraction methods for soil metals, a set of stepwise multiple linear regression models with the New Zealand region as the categorical variable were employed to evaluate the relationships between plant Cd and environmental factors, since the predictive power of any of the Cd bioavailability tests by itself was not very good. As shown in Table 3.6, regression models to predict Cd concentration varied between plants species and the effect of region was significant in each model. The regression model with maximum R^2_{adj} for onion Cd (59.6%) was related to the explanatory variable soil $Ca(NO_3)_2$-Cd. Likewise, the multiple regression models with the best fit for spinach Cd also indicated the dominant role of soil $Ca(NO_3)_2$-Cd in spinach Cd uptake, which explained 77.1% of total variation. A combination of climatic variables (air average temperature), $^{Cd}C_{DGT}$ and soil total P concentration explained 76.5% of total variation in potato Cd. Olsen-P, porewater Cd and plant Zn concentration accounted for 57.9% of the variation in wheat Cd concentration.

Table 3.6 Multivariate regression analysis for plant Cd concentrations

Model	Region	Regression equation	Adjusted R^2
log(Onion- Cd)	Auckland	- 0.46 + 0.12 log($Ca(NO_3)_2$-Cd)	0.596
	Canterbury	- 0.88 + 0.12 log($Ca(NO_3)_2$-Cd)	
	Hawkes Bay	- 1.32 + 0.12 log($Ca(NO_3)_2$-Cd)	
	Waikato	- 0.72 + 0.12 log($Ca(NO_3)_2$-Cd)	
log(Potato- Cd)	Auckland:	- 0.02 + 2.84 log (Air temperature) + 0.04 log(DGT-Cd) - 1.19 log (Total P)	0.767
	Canterbury:	- 0.86 + 2.84 log (Air temperature) + 0.04 log(DGT-Cd) - 1.19 log (Total P)	
	Manawatu-Whanganui	- 0.37 + 2.84 log (Air temperature) + 0.04 log(DGT-Cd) - 1.19 log (Total P)	
	Waikato:	- 0.28 + 2.84 log (Air temperature) + 0.04 log(DGT-Cd) - 1.19 log (Total P)	
log(Spinach- Cd)	Auckland:	- 0.43 + 0.003 Olsen- P + 0.27 log($Ca(NO_3)_2$-Cd)	0.765
	Gisborne:	- 0.33 + 0.003 Olsen- P + 0.27 log($Ca(NO_3)_2$-Cd)	
	Manawatu-Whanganui:	- 0.30 + 0.003 Olsen- P + 0.27 log($Ca(NO_3)_2$-Cd)	
	Tasman:	- 0.20 + 0.003 Olsen- P + 0.27 log($Ca(NO_3)_2$-Cd)	
	Waikato:	- 0.35 + 0.003 Olsen- P + 0.27 log($Ca(NO_3)_2$-Cd)	
log(Wheat- Cd)	Canterbury	0.58 - 0.51 log(Olsen-P) + 0.08 log(porewater-Cd) - 0.80 log(plant Zn)	0.579
	Manawatu-Whanganui:	0.63 - 0.51 log(Olsen-P) + 0.08 log(porewater-Cd) - 0.80 log(plant Zn)	

3.4 Discussion

3.4.1 Relationships between plant cadmium concentration and environmental factors

The significant correlation between Cd concentrations in spinach and soil pH agrees with other studies (Al Mamun et al., 2016; Gray et al., 1999d; Loganathan et al., 2003). They suggested that soil pH was the dominant soil factor controlling Cd availability. Under acidic conditions, Cd desorption from soil colloids is strongly promoted and therefore soil Cd is more bioavailable due to the increase of Cd^{2+} hydrolysis and competition from protons or acidic metal cations for binding sites (Loganathan et al., 2012). The reason why similar correlations are not seen between pH and Cd concentrations in other plants, may be because of other factors that affect the solubility of Cd in these soils. This was also observed by Reiser et al. (2014) when looking at Cd concentration in pasture plants. Meanwhile, soil total carbon concentration played a non-significant role in reducing plant Cd in this study. This was different from some reports indicating the negative effects of soil organic C on Cd uptake by plant (Al Mamun et al., 2016; Al Mamun et al., 2017). The poor correlations between plant Cd concentration and soil carbon content were likely due to the non-significant effects of soil total C on

the solubility of soil Cd. The $Ca(NO_3)_2$ (R = 0.22, P < 0.05) and DGT (R= 0.15, P > 0.05) extracted Cd concentrations were positively correlated with soil total C concentration (not shown). Gray et al. (1999d) investigated the Cd solubility in 29 NZ soils spanning 10 out of NZ's 15 soil orders with widely ranging soil properties and found that there was no significant correlation between soil organic C and with $Ca(NO_3)_2$ extracted soil Cd concentration. A similar non-significant relationship between Cd concentration in weak salt extraction (and plants) and soil organic C also reported in pasture systems by Reiser et al. (2014). This implies that some other soil factors rather than soil C concentration play an important role in determining soil Cd bioavailability, for example, soil type. Bolan et al. (2003a) reported allophanic soils had higher pH and greater amounts of negative charge and Cd^{2+} absorption compared to non-allophanic soils. In our study, a large number of samples were collected from the Waikato region, which is dominated by volcanic soils (*i.e. Allophanic* and *Granular Soils* (Hewitt, 2010)). The high Cd concentration in soils but low Cd concentration accumulated in plants was observed by Cavanagh et al. (2016) who found that the Cd concentration in potatoes grown in Canterbury was two times higher than that in Waikato (P < 0.05) while the Cd concentration in soil in Canterbury was four-fold lower than that in Waikato. In contrast to the Waikato, Canterbury is mainly dominated by Sedimentary soils (*i.e. Brown* and *Pallic Soils* (Hewitt, 2010) with low soil pH and organic C concentration, contributing to a high bioavailability of soil Cd . This may explain the high PUF in Canterbury. A positive effect of air temperature and negative of soil total Cd and P concentration on Cd uptake by potatoes may also be attributable to a region effect. Generally, potato seed is sown in October in Canterbury, around one to two months later than that in Waikato or Auckland. This may result in a relatively similar or even higher average air temperature (particularly air temperature on the day) in Canterbury during the growing season of potato (Table 4.1 in chapter 4). The positive correlation between rainfall and Cd concentration in onion and spinach may be due to the rainfall-induced decline in soil pH, which may increase soil Cd availability (Reiser et al., 2014).

Due to the chemical similarity, the relation of Cd and Zn and their uptake by plants is well documented, including both synergistic and antagonistic effects (McLaughlin et al., 2011). Cd and Zn accumulation in potato tuber in this study exhibited positive correlations, indicating a synergistic effect between these two elements (P < 0.05). This agrees with previous findings by (Ashrafzadeh et al., 2017), who indicated the uptake of Cd and Zn in potato grown in soils from Canterbury were significantly correlated. Similar synergistic interaction between plant Cd and Zn was also observed in spinach leaf, while Cd and Zn concentration in wheat grain indicated a strong antagonistic interaction (P < 0.01). Wheat grain Zn concentration in the collected samples was significantly higher than potato tuber Zn (P < 0.05) (Figure B1 in Appendix), and the responding PUF of wheat Zn

(average 0.29) was also higher than potato (0.18) with a significant difference ($P < 0.01$) (Figure 3.4). A greater requirement of Zn, an essential micronutrient, in wheat grain might promote Cd uptake if there is potential soil Zn-deficiency, which had been reported in Canterbury (Haynes, 1997; McLaren et al., 1984). This agrees with previous findings which showed that Zn application could effectively reduce wheat Cd concentration (Qaswar et al., 2017; Sarwar et al., 2015).

3.4.2 Relationships between plant cadmium concentration and soil Cd measurements

This study highlights the importance of the effect of region (site) when attempting to assess capabilities of different methods for predicting Cd accumulation in plants. This agrees with Pérez and Anderson (2009) who successfully employed site-specific multiple regression models which integrated $^{Cd}C_{DGT}$ and soil properties to explain Cd uptake by potato and wheat. Incorporating the effect of region, the predictive power of $Ca(NO_3)_2$ extracted Cd to predict Cd concentration in onion bulbs was improved to 59.6% in the multiple regression model. Of the four plant species, spinach had the highest single regression line gradients (R^2_{adj}). This may be due to the movement of Cd within spinach induced by transpiration via water transport without the transfer of Cd from xylem to phloem (McLaughlin et al., 2011). Multiple regression models showed that Cd concentrations in spinach leaves were related to Olsen P and $Ca(NO_3)_2$ extractable Cd concentrations, indicating that fertiliser status has to be taken into consideration when using the $Ca(NO_3)_2$ extractant to assess Cd uptake by spinach. The regression models for estimating Cd enrichment in potato tubers and wheat grain had more explanatory variables. This may be because the movement of Cd in 'fruiting' vegetables (potato and wheat) is more complicated than for leafy vegetables due to the influence of bio-membranes on Cd translocation within plants (McLaughlin et al., 2011). This implies that more factors have to be included when predicting Cd accumulation in 'fruiting' vegetables, such as the high transpiration rate (Tani & Barrington, 2005) and the translocation of Cd between plant tissues (Stritsis & Claassen, 2013). The responses of potato and wheat to soil variables, climate factors and the measured phyto-avaiable soil Cd were different. The mechanism behind the ability of different plant species to mobilise Cd involves many biochemical processes, such as the alternation of soil pH (Zaccheo et al., 2006), the releasing of root exudates (Lu et al., 2007), and the symbiotic association with rhizobia bacteria and mycorrhiza (Uroz et al., 2009). These biochemical processes may influence the accurate estimation of soil Cd bioavailability by these four methods. In addition to the use of soil properties, air temperature was included in the estimation of potato Cd concentration. This is consistent with findings by Reiser et al. (2014) indicating that climate was an important explanatory variable when estimating Cd concentration in NZ pasture plants. When looking at Cd uptake by wheat, only Cd concentration in porewater was positively correlated to grain Cd concentration,

which explained 17.2% of the variation of grain Cd. This confirmed the findings in a previous study by Gray et al. (2001) who found no significant correlation between soil extracted Cd concentrations and Cd concentrations in winter wheat grain samples collected from NZ field trials. In another field survey on wheat heavy metal accumulation, Nan et al. (2002b) reported no meaningful explanatory variables to account for the variation of metal accumulation in wheat grain under field conditions, and they indicated that the uptake of metals by plants could be mainly influenced by the crop's physiological characteristics. The integration of region, soil Olsen P, porewater Cd and plant Zn concentration significantly accounted for the most variation in Cd uptake by wheat in our study, which is consistent with Black et al. (2014) who suggested that plant responses should be taken into consideration when assessing the bioavailability of soil metals for wheat. Various relationships between plant Cd concentration and measured Cd bioavailability indicated that the applicability of soil extractants on the prediction of Cd uptake by plant was species dependent (Almås et al., 2006).

In this study, all extractable soil Cd measurements were positively correlated to soil total Cd ($P < 0.01$) (Table B3 in Appendix). This was different from other soil surveys in NZ (Gray et al., 1999d; Reiser et al., 2014) which showed non-significant correlations between $Ca(NO_3)_2$ extractable Cd and total Cd concentrations in the soil survey. The difference may be due to a much larger number of soil samples in this study. Generally, the DGT technique mimics a kinetic metal absorption flux by plants and quantifies the exchange kinetics between solid phase and solution, rather than just reflecting the equilibrium state of soil metals (Zhang et al., 1998), and has successfully estimated Cd uptake by plants in some studies (Black et al., 2011; Williams et al., 2012). However, no significant linear relationships between the $^{Cd}C_{DGT}$ and Cd concentration were observed in spinach, onion and potato. Looking at the ratio (R) between $^{Cd}C_{DGT}$ and soil solution Cd, a low value of R implied there was very little solution Cd supplied from the exchangeable solid phase during the deployment. Similar low R values in non-spiked soils under field conditions were also reported in some studies (Dočekalová et al., 2015; Senila et al., 2012). The low available Cd concentration of the non-spiked field soils may affect the accuracy of DGT in predicting Cd bioavailability. Similar low correlations between $^{Cd}C_{DGT}$ and plant Cd concentration were reported in some other NZ studies (Black et al., 2012a; Black et al., 2012b), indicating that $^{Cd}C_{DGT}$ provided the lowest regression line gradients (R^2_{adj}) when estimating Cd accumulation in plants in biosolids amended metal-spiked soils compared to soil total Cd, EDTA, $Ca(NO_3)_2$, soil solution and free Cd^{2+} activity. Particularly, the Cd concentration in wheat grain negatively correlated to $^{Cd}C_{DGT}$ ($P < 0.05$) in this study, in line with the finding of Black et al. (2014) in a pot experiment, highlighting that sole chemical or passive diffusion methods were inadequate to estimate Cd uptake by plants. This also supported the conclusion made by Black et al. (2012a) that $Ca(NO_3)_2$ had a higher predictive power in the assessment of Cd bioavailability of soils across soil

types. This may be because $Ca(NO_3)_2$ extraction can sample a larger pool of Cd from the solid phase that the plants can access through (e.g.) exudates and release from SOM (by promoting microbial action or preferentially growing roots in nutrient rich areas of soil), compared to the DGT technique which is much more sensitive to the effect of diffusive limitation in the soils (Degryse et al., 2009).

However, from a predictive perspective, the values of R^2_{adj} of each multiple regression model in our study are comparatively lower, compared with some studies conducted in pot experiments (Dai et al., 2018; Song et al., 2015) or in deeper soil horizons (Yang et al., 2016). This may also be due to the discrepancy between soil sampling horizons and actual depth of root placement. Thorup-Kristensen (1999) found that the crops' rooting system was influenced by the duration of growth. Due to a short growing season, spinach might have a shallow root system when harvested, which may support its highest R^2_{adj} in a single linear model (Schenk et al., 1991). In comparison to leafy vegetables, a much longer growing duration probably contributed to a deeper root placement for potato and wheat, which were mainly distributed in the 0 - 40 cm soil layer under the field conditions (Thorup-Kristensen, 1999; Wang et al., 2006b; Zhang et al., 2004). In terms of potato root systems, Wang et al. (2006b) found that the top 10 cm soil layer only contained 26 - 41% of root length density, although it had 63 - 82% of total root weight density. This means that there are a considerable amount of fine roots distributed in the deeper soil horizons. It is documented that fine roots play an important role in water and mineral uptake (including heavy metals) (Gordon & Jackson, 2000; Gussarsson, 1994; Weis & Weis, 2004).

3.5 Conclusion

The aim of this study was to investigate the decisive factors driving the Cd concentrations in onion, potato, spinach and wheat. The PUF values of each crop species exhibited a variability of Cd transfer from soil to plant varying between regions due to different soil properties and climatic conditions. Many environmental factors revealed significant correlations with Cd concentrations in plants. The bioavailability testing showed that the predictive capability of these four methods (pseudo-total Cd concentration, 0.05 M $Ca(NO_3)_2$ extractable Cd, the DGT measured Cd and porewater Cd) varied between plants. Multivariate regression analysis showed that once certain soil and climatic variables were accounted for, $Ca(NO_3)_2$ extractions could provide a satisfactory prediction of Cd uptake by onions and spinach, while Cd accumulation in potato tuber and wheat grain are affected by various environmental variables including soil variables, fertiliser status, climatic condition and plant Zn concentration. The results indicated that various environmental factors can combine to determine the uptake of Cd by different crop species and should be considered when estimating the risks posed

by Cd in agricultural soils. Also, sampling soil from the top 15 cm horizon may not be enough to assess the Cd uptake by plants, especially for crops with a long growth duration.

Chapter 4

Effect of lime and compost amendments on cadmium uptake by potato and wheat under field conditions

A manuscript from this chapter has been prepared to submit to the *Journal of Environmental Quality*.

My contribution to this article: I helped set up and monitored the field trials, collected soil and plant samples and completed the laboratory work with the help of my co-authors. I collated and analysed the data and developed the original draft of the manuscript.

4.1 Introduction

Unlike organic pollutants, Cd does not undergo chemical or microbial degradation, therefore, it can persist in situ for a long duration after its introduction into the soil environment (Mahar et al., 2015). Controlling the risk presented by soil Cd contamination in agricultural systems often involves limiting its bioavailability by reducing its solubility. In situ chemical immobilisation by the addition of amendments to decrease successfully the Cd uptake by plants has been well documented in some studies (Gray et al., 2006; Liu et al., 2009). These amendments often include inorganic agents such as lime (Bolan et al., 2003b; Valentinuzzi et al., 2015), phosphate compounds (Bolan et al., 2003a), iron and manganese oxides (Chen et al., 2000) and organic materials such as biosolids (Black et al., 2012b), lignite (Al Mamun et al., 2016; Simmler et al., 2013), and compost (Al Mamun et al., 2017; van Herwijnen et al., 2007). Apart from reducing Cd mobility and phytotoxicity, some materials used for heavy metal immobilization are well-known for their cost-effectiveness and the capacity to improve soil fertility. For instance, liming soils with low pHs can ameliorate soil acidity, eliminate Al^{3+} and Mn^{2+} toxicity and improve nutrient bioavailability (Bolan et al., 2008; Sparrow et al., 1993). The application of C-rich materials can benefit the physical, chemical and biological characteristics of soil by supplying plant nutrients, reducing the application of mineral fertiliser, enhancing soil carbon sequestration and increasing soil porosity to improve moisture holding capacity and decrease soil density (Khan et al., 2017).

The mechanisms behind these amendments' ability to reduce soil Cd bioavailability mainly involve the alteration of soil pH and increase of cation binding sites, by influencing Cd hydroxyl speciation in

soil solution (Bolan et al., 2003b; Valentinuzzi et al., 2015), or increasing Cd sorption by soil colloids (Al Mamun et al., 2016; Al Mamun et al., 2017). However, the effects of amendments on the reduction of Cd uptake by plants are not consistent between these studies and can depend on the application rates (Simmler et al., 2013), types of amendments (Al Mamun et al., 2016), plant species and cultivars (Benyas et al., 2018), and soil variables (*e.g.* soil types, soil pH and soil organic matter content) (Gray et al., 1999c). Moreover, most of these studies on soil Cd remediation have been conducted in pot trials under greenhouse conditions, rather than in the field. Maier et al. (1996) found that liming significantly reduced Cd concentration in potato tubers in a pot trial, but had no or even opposite effects in field conditions. A similar discrepancy between pot and field experiments was also reported in barley grain (Friesl et al., 2006). Compared to field conditions, pot trials have more homogeneous distribution of soil variables and larger root density, which may contribute to more interaction between the soils and roots and consequently accentuate the effects of additional amendments on plant Cd uptake. Thus, pot experiments cannot fully replace field trials to evaluate the effectiveness of soil Cd amendments and may not provide a guarantee of safe Cd remediation for agricultural products under nature field circumstances (Sun et al., 2016). Field assessments of the efficacy of soil amendments to reduce Cd uptake by crop plants, are essential to conclusively understand the effects of different environment variables on mitigating potential risks from the metal.

Potato and wheat are staple foods in NZ. It has been reported in some NZ studies that the Cd concentrations in these two plants may exceed the maximum limit in the Food Standard of Australia and New Zealand (FSANZ, 0.1 mg kg^{-1} (fresh weight, FW)) (Gray et al., 2001; Kim, 2005). Gray et al. (2001) reported that 10 % of wheat grain samples had Cd concentrations higher than the 0.1 mg kg^{-1} (FW) maximum permissible limit, and Kim (2005) estimated that around 1.5% of the potato samples in the Waikato exceeded that concentration. The same problem of Cd concentration in these plants exceeding the maximum permissible limit occurs internationally. In Australia, McLaughlin et al. (1997a) showed that Cd concentrations in potato tuber (n = 352) varied between 0.004 and 0.232 mg kg^{-1} (FW), with 5.0% exceeding 0.1 mg kg^{-1}. In Kunshan City, a developed area in Yangzi River Delta of China, wheat grain samples had Cd concentrations ranging from 0.006 to 0.179 mg kg^{-1}, with 25% higher than the tolerance limit of the Chinese standard of wheat (0.1 mg kg^{-1}, dry weight, DW) (Huang et al., 2008). Therefore, the development of strategies to reduce the risk of human exposure to soil Cd with the intention of preventing Cd concentrations from exceeding the guideline values in the edible parts of these two crops are imperative. Although the effects of some soil amendments such as lime, biosolids and compost on Cd uptake by wheat and potato have been tested in NZ,, such studies have not been conducted with field trials, and potential effects of environmental variability

(soil types and climate conditions) on a regional scale have also not taken into consideration. The aim of this chapter was to assess the potential of lime and compost for the reduction of Cd uptake by these two crops under field conditions. This was investigated by evaluating the effects of different application rates of lime and compost on Cd availability in soils and its accumulation in plants.

4.2 Methods and materials

4.2.1 Study sites

From August 2016 to April 2017, three potato field trials were undertaken in Pukekohe, Manawatu, and Canterbury, which are main potato growing regions in NZ. Between May 2015 and January 2017, a wheat trial was carried out in Canterbury. During the growing period, average air temperature ranged from 14.6 °C to 16.63 °C for the three potato trials, while the wheat trial in Canterbury was 11.41 °C. The Pukekohe and Manawatu sites had more rainfall (total rainfall at 500 and 560 mm respectively) than the two Canterbury sites. The details of climatic conditions of these trials were shown in Table 4.1 while the corresponding soil physical and chemical properties were shown in Table 4.2.

4.2.2 Experimental Design

Each trial was laid out in a randomized block design which consisted of 30 plots (4 × 3.4 m^2 in potato trials and 3 × 1.6 m^2 in the wheat trial) to which 10 treatments were applied in triplicate(Table 4.3). In each trial, each plot had one of five pH levels varying from 5.3 to 7.0, which was achieved by applying commercial lime (*Aglime*, 98% $CaCO_3$, *Ravensdown Fertiliser Co-operative Ltd.*) or fine elemental sulphur (*Kumulus, BASF New Zealand Ltd.*), depending on the initial soil pH. Before the application of lime, an initial soil sample was taken and incubation studies were carried out as part of a separate research project (Thompson-Morrison, 2017) to determine the rates of lime applied. With certain exceptions (see below), at each soil pH, compost (from *Living Earth Christchurch*) was added at rates of 0 and 25 t ha^{-1} as separate treatments. Compost was not applied to the sulphur treatment (Pukekohe potato trial) or the highest lime rate treatment in the Manawatu and Canterbury potato trials. In addition, a larger amount of compost (50 t ha^{-1}) was applied when no pH amendment (lime) was added in the potato trials. Liming is a common practice in wheat farming on the Canterbury Plains, where the Canterbury sites were located, due to the natural low soil pH. Hence, the application of compost at 50 t ha^{-1} in the wheat trial was applied in the treatment which had the lowest liming rate. The details of amendments application are described in Table 4.3.

The amendments were spread evenly over the surface of each plot and thoroughly mixed with the soil and ploughed using a mechanized rotary tiller (30 - 40 cm depth). For the potato trials, two buffer rows of potatoes were established around the field trial. Potatoes were planted one month after the application of soil amendments. Four rows of potatoes (cultivar *Moonlight*) were grown in each plot with 0.8 m spacing between rows and a 0.3 m spacing between plants in a row. Six cores of soil were collected from the inner 2 row × 2 m^2 area of each plot one day before potato seeds were sown. Another six cores of soil were collected at the time of harvest. The layout of the potato trials and the setup of each plot are shown in Figures C1 and C2 (Appendix). In this study, the growth period of potatoes was around five months. Due to different climatic conditions at the three sites, each potato trial had different sowing times (Table 4.1).

A wheat (cultivar, Reliance) trial was also established near the Canterbury potato trial with similar soil properties and climatic conditions. Similar treatments were applied (Table 4.3). The single plot area was smaller (3 × 1.6 m^2) with only 1 m buffer between plots. Nine rows of wheat were grown in each plot with 0.2 m spacing between rows. Five soil cores were sampled from the inner 1 m^2 area of each plot immediately before planting and after harvesting (Figures C3 and C4 in Appendix). The wheat had been grown for 7.5 months before harvesting in January 2017.

All potato tubers and wheat grains within the inner area (2 rows × 2 m for the potato trials and 1 m × 1 m for the wheat trial) of each plot were harvested. Before harvesting, five potato tubers from five different plants were initially collected as representative subsamples for lab analysis. The remaining potatoes were harvested to determine yield. Wheat heads in the inner area of each plot were harvested, air-dried for several days and milled to yield the grain. After that, a representative sub-sample (around 200 g) from each plot was kept for chemical analysis.

Table 4.1 Location and climatic conditions of the field trials and the date that crops were planted and harvested.

Field trial	Latitude	Longitude	[a] Climate agent No.	Average air temperature (°C d^{-1})	Total rainfall (mm)	Radiation (MJ m^{-2} d^{-1})	Date planted	Date harvested
Pukekohe potato	37° 20′ 41′′ S	174° 58′ 39′′ E	2006	14.60	500	16.44	17/08/2016	17/01/2017
Manawatu potato	40° 20′ 12′′ S	175° 28′ 11′′ E	3243	16.63	560	18.14	8/11/2016	10/04/2017
Canterbury potato	43° 38′ 16′′ S	172° 27′ 22′′ E	17603	15.29	224	20.05	13/10/2016	22/03/2017
Canterbury wheat	43° 38′ 17′′ S	172° 27′ 26′′ E	17603	11.41	271	14.05	09/06/2016	24/01/2017

[a] Climate agent number used in the National Institute of Water and Atmospheric Research (NIWA) represents for the serial number (ID) of each climate station.

Table 4.2 Chemical properties for the background soils in the four trials and the compost that was applied in this study.

Field trial	Material	Soil types	pH	Total C %	CEC me $100g^{-1}$	Silt %	Clay %	Total P mg kg^{-1}	Total Al mg kg^{-1}	Total Fe mg kg^{-1}	Total Cd mg kg^{-1}	Total Zn mg kg^{-1}
Pukekohe potato	Soil	Orthic Granular	6.1	2.91	17	28	61	1995	117803	57240	0.47	81.95
Manawatu potato	Soil	Orthic Gley	5.3	1.96	13	52	20	562	29584	17453	0.11	49.18
Canterbury potato	Soil	Typic Immature Pallic	5.6	2.24	12	56	20	257	29049	17099	0.16	59.40
Canterbury wheat	Soil	Typic Immature Pallic	5.3	2.16	12	48	18	564	18231	15435	0.23	50.69
	Compost	--	7.2	27.80	45	--	--	5142	13064	14496	0.48	327.58

Table 4.3 Amendment application rates in the four experimental trials.

Pukekohe potato trial (t ha^{-1})					Manawatu & Canterbury potato trial (t ha^{-1})					Canterbury wheat trial (t ha^{-1})				
Treatments		Target pHs	Lime	MC [a]	Treatments		Target pHs	Lime	MC	Treatments		Target pHs	Lime	MC
pH- 1	MC-0	5.6	1.1 [b]	0	pH- 1	MC-0		0	0	pH- 1	MC-0	5.3	0	0
	MC-0		0	0		MC-25	5.6	0	25		MC-0		2.3	0
pH- 2	MC-25	6.0	0	25		MC-50		0	50	pH- 2	MC-25	5.6	2.3	25
	MC-50		0	50	pH- 2	MC-0	6.0	4.2	0		MC-50		2.3	50
pH- 3	MC-0	6.4	4.2	0		MC-25		4.2	25	pH- 3	MC-0	6.0	4.4	0
	MC-25		4.2	25	pH- 3	MC-0	6.3	7.2	0		MC-25		4.4	25
pH- 4	MC-0	6.7	9.0	0		MC-25		7.2	25	pH- 4	MC-0	6.3	7.9	0
	MC-25		9.0	25	pH- 4	MC-0	6.7	12.0	0		MC-25		7.9	25
pH- 5	MC-0	7.0	13.8	0		MC-25		12.0	25	pH- 5	MC-0	6.6	11.3	0
	MC-25		13.8	25	pH- 5	MC-0	7.0	18.0	0		MC-25		11.3	25

[a] MC = municipal compost from *Living Earth, Christchurch*.

[b] The amount of applied sulphur amendment.

4.2.3 Plant analysis

Each potato tuber (subsample) was rinsed three times with tap water, followed by rinsing with deionized water (DI, 18.2 MΩ-cm) several times. They were then peeled using a clean potato peeler and only the central starchy part of the tubers were used and cut into small pieces a clean stainless steel knife, prior to being oven-dried at 60 °C. The wheat subsamples were oven-dried at 60 °C to constant weight before chemical analysis.

The potato and wheat sub-samples were ground to fine powders with a grinder (A10 Analytical Grinder, Yellowline by IKA) before being stored in air-tight polyethene containers. Each sample was digested with 4 mL HNO_3 (50:50, v/v) and 2 mL H_2O_2 in a microwave digest (MARSXPRESS, CEM Corp.). The digests were subsequently diluted with DI water to a final volume of 10 mL. The digests were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 720 ES – USA) for Cd and Zn concentrations.

4.2.4 Soil analysis

Soils collected from the inner area of each plot were air-dried for around 10 days at room temperature and then passed through a 2 mm plastic sieve before chemical analysis. Soil samples (10 g) were put into a tube with 25 mL DI water at a solid/water ratio of 1:2.5. After being shaken for 30 minutes, the mixture was left to equilibrate for 8 hours and then was tested with a Mettler Toledo pH meter (Mettler Toledo Seven Easy) (Blakemore & Price, 1987). Total carbon (C) and nitrogen (N) were measured using an Elementar Vario MAX CN element analyser. The cation exchange capacity (CEC) and base saturation (BS) of soils were measured using the Silver Thiourea (AgTU) following the method in Blakemore et al. (1987). Briefly, soil (0.7 g) was added to a 50 centrifuge tube with 35 mL of 0.01 M Silver Thiourea (AgTU), and then agitated for 16 h in an end-over-end shaker. After being centrifuged at 2000 rpm for 10 minutes, the supernatant was filtered (Whatman No. 40) and analysed using ICP-OES.

The bioavailable fraction of soil Cd was estimated based on the 0.05 M calcium nitrate extraction method used by Gray et al. (1999b) (forthwith, "$Ca(NO_3)_2$-extractable Cd") . Soil samples (5 g) were weighed into a centrifuge tube with 30 mL of extractant. Tubes were agitated for 2 h on an end-over-end shaker, centrifuged for 10 min at 3300 rpm, and filtered using a Whatman 52 filter paper. Final extractions were analysed to determine Cd and Zn concentration using inductively coupled plasma – mass spectrometry (ICP-MS, Agilent-7500cx).

The pseudo-total soil metal and P concentrations (forthwith, 'total' concentrations for simplicity) were analysed using concentrated acid digests following the method of (Simmler et al., 2013). Briefly, 0.5 g soil was digested in 3 mL trace element grade nitric acid (HNO_3, > 65%) and 3 mL hydrogen peroxide (H_2O_2, 30%). The digest was made to 25 mL with DI water and filtered with a Whatman 52 filter paper. The soil digests were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for Cd and ICP-OES for other metals and P.

4.2.5 Quality control

A duplicate test was used in every 20 samples to assess the repeatability of the analysis. Several internal and external certified soils (NIST Montana 2711; Interlab internal WEPAL soil 921; Interlab internal WEPAL soil 981), and plant reference samples (NIST 1573a, tomato leaves; ASPAC internal clover; ASPAC internal beetroot) were used as standard reference materials to assess the accuracy of the metals analysis. The recovery ratios of the standard soils varied from 96 - 106% for Cd and 92 - 93% for Zn, while standard plants ranged between 92 - 96 % for Cd and 103 - 105% for Zn.

4.2.6 Statistical analysis

The mean Cd concentration of plants and soils were compared between treatments in each field trial with a one-way ANOVA using Duncan's Test at the 0.05 level of significance. The effects of liming, compost addition and their interaction on plant yield, soil pH and total C concentration, Cd concentration in $Ca(NO_3)_2$ extracts and plants were analysed with a two-way ANOVA using the R package *agricolae* (De Mendiburu, 2014). In terms of Cd concentration in potato, a three-way ANOVA analysis was conducted to evaluate the effects of liming, compost, site (region) and their interaction using the R package *agricolae*. Correlations between plant Cd concentration and soil variables (including soil pH, total carbon and nitrogen concentration, total Cd and Zn concentration, CEC, $Ca(NO_3)_2$ extractable Cd and Zn concentration), and between Cd and Zn concentration in plants were analysed using Pearson correlation coefficients.

4.3 Results

4.3.1 Effects of amendments on soil pH, total C and total Cd concentrations

Soil pH was affected by liming (and sulphur in Pukekohe) ($P < 0.001$) in all field trials (Table 4.4). Similarly, soil total C was significantly increased by compost application in four trials while lime addition did not impact soil C concentration significantly. Meanwhile, compost application slightly increased surface soil pH at low soil pH conditions, but the effect was only significant in the

Manawatu trial. The application of amendments did not affect soil Cd concentrations significantly at any of the trials (Table C1 in Appendix). The effect of the interaction between compost and lime on soil properties did not significantly affect soil pH and total C, except for soil pH in the Manawatu potato trial.

Table 4.4 The effects of applied amendments on soil pH and total C content in four experimental trials.

Pukekohe potato trial Treatments		soil pH	Soil total C (%)	Manawatu potato trial Treatments		soil pH	Soil total C (%)
pH- 1	MC-0	5.64 ± 0.04 f	2.88 ± 0.04 abc	pH- 1	MC-0	5.31 ± 0.02 g	1.96 ± 0.04 def
pH- 2	MC-0	6.14 ± 0.18 e	2.91 ± 0.03 ab		MC-25	5.56 ± 0.04 f	2.19 ± 0.02 bc
	MC-25	6.31 ± 0.14 de	2.86 ± 0.07 bc		MC-50	5.82 ± 0.09 e	2.44 ± 0.13 a
	MC-50	6.24 ± 0.12 de	2.95 ± 0.04 a	pH- 2	MC-0	6.26 ± 0.08 d	2.04 ± 0.05 cdef
pH- 3	MC-0	6.55 ± 0.14 cd	2.68 ± 0.09 c		MC-25	6.27 ± 0.04 c	2.13 ± 0.08 bcde
	MC-25	6.82 ± 0.11 bc	2.82 ± 0.06 bc	pH- 3	MC-0	6.71 ± 0.09 bc	1.91 ± 0.02 f
pH- 4	MC-0	7.01 ± 0.02 ab	2.74 ± 0.09 bc		MC-25	6.64 ± 0.05 c	2.13 ± 0.06 bcd
	MC-25	7.04 ± 0.06 ab	3.11 ± 0.07 bc	pH- 4	MC-0	6.90 ± 0.05 a	1.93 ± 0.07 ef
pH- 5	MC-0	7.24 ± 0.08 a	2.85 ± 0.13 bc		MC-25	6.81 ± 0.06 abc	2.26 ± 0.06 ab
	MC-25	7.20 ± 0.07 a	2.93 ± 0.08 ab	pH- 5	MC-0	6.86 ± 0.02 ab	2.01 ± 0.04 cdef
Analyses of variance		F-values	F-values	Analyses of variance		F-values	F-values
pH		53.32 ***	1.7	pH		205.69 ***	1.7
MC		1.04	3.43 *	MC		14.34 ***	3.43 *
pH × MC		0.79	2.7	pH × MC		3.45 *	2.7
Canterbury potato trial Treatments		soil pH	Soil total C (%)	Canterbury wheat trial Treatments		soil pH	Soil total C (%)
pH- 1	MC-0	5.60 ± 0.03 d	2.24 ± 0.06 ef	pH- 1	MC-0	5.27 ± 0.05 c	2.16 ± 0.03 ab
	MC-25	5.84 ± 0.15 d	2.38 ± 0.04 bcdf	pH- 2	MC-0	5.97 ± 0.19 b	2.01 ± 0.07 b
	MC-50	5.78 ± 0.06 d	2.60 ± 0.05 a		MC-25	6.23 ± 0.22 ab	2.29 ± 0.12 ab
pH- 2	MC-0	6.63 ± 0.05 bc	2.21 ± 0.02 f		MC-50	6.43 ± 0.32 ab	2.42 ± 0.13 a
	MC-25	6.60 ± 0.16 c	2.46 ± 0.07 abcde	pH- 3	MC-0	6.41 ± 0.27 ab	2.03 ± 0.09 b
pH- 3	MC-0	6.79 ± 0.09 abc	2.29 ± 0.03 ef		MC-25	6.37 ± 0.12 ab	2.23 ± 0.07 ab
	MC-25	6.77 ± 0.06 abc	2.51 ± 0.01 abcd	pH- 4	MC-0	6.56 ± 0.26 ab	2.03 ± 0.15 b
pH- 4	MC-0	7.01 ± 0.00 a	2.38 ± 0.08 cdef		MC-25	6.62 ± 0.18 ab	2.34 ± 0.11 ab
	MC-25	6.91 ± 0.06 ab	2.59 ± 0.08 ab	pH- 5	MC-0	6.81 ± 0.25 a	2.17 ± 0.06 ab
pH- 5	MC-0	7.01 ± 0.11 a	2.58 ± 0.15 abc		MC-25	6.63 ± 0.14 ab	2.24 ± 0.09 ab
Analyses of variance		F-values	F-values	Analyses of variance		F-values	F-values
pH		76.08 ***	2.66 *	pH		8.87 ***	0.42
MC		0.18	15.31 ***	MC		0.82	7.17 **
pH × MC		1.34	0.24	pH × MC		0.38	0.63

Data in the table shows the means of three replicates ± standard error, and the same letters between treatments in each column stand for non-significance at the 5% level. Significance levels of lime, compost and the interaction Lime × compost are indicated: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

4.3.2 Effects of amendments addition on soil metal solubility

The $Ca(NO_3)_2$ extractable Cd decreased with the increase of soil pH (Table 4.5). Within each trial, treatment with the lowest soil pH had the largest amount of $Ca(NO_3)_2$ extractable Cd. Lime addition (and sulphur in Pukekohe) significantly affected soil bioavailable Cd at all trials. In the case of no compost addition, the treatment with the highest soil pH had the smallest amount of soil $Ca(NO_3)_2$ extractable Cd concentration, being 90.8%, 91.8%, and 93.1% lower than that in the treatment with the lowest soil pH in the Canterbury wheat trial, Manawatu potato trial, and Canterbury potato trial, respectively. Likewise, compost also significantly influenced the availability of soil Cd at all sites, except in Pukekohe. However, the reductions of soil extractable Cd concentration induced by compost addition depended on soil pH. There was a tendency for compost application decreasing the concentration of $Ca(NO_3)_2$ extractable Cd in the low soil pH treatments while there were no effects at high pH treatments.

Table 4.5 The effects of applied amendments on soil $Ca(NO_3)_2$ extractable Cd concentrations in the four field trials.

Pukekohe potato trial Treatments		$Ca(NO_3)_2$-Cd (μg kg^{-1})	$Ca(NO_3)_2$-Zn (μg kg^{-1})
pH- 1	MC-0	57.83 ± 15.36 a	210.96 ± 39.63 a
pH- 2	MC-0	34.75 ± 7.78 ab	102.66 ± 25.14 bc
	MC-25	27.41 ± 2.98 b	77.49 ± 21.14 bcd
	MC-50	37.7 ± 10.57 ab	126.87 ± 18.1 b
pH- 3	MC-0	30.37 ± 9.56 ab	52.84 ± 11.16 cd
	MC-25	22.25 ± 3.93 b	47.53 ± 18.63 cd
pH- 4	MC-0	33.19 ± 10.59 ab	42.87 ± 3.64 d
	MC-25	18.93 ± 1.27 b	34.4 ± 7.52 d
pH- 5	MC-0	32.45 ± 9.68 ab	43 ± 8.34 d
	MC-25	20.73 ± 2.69 b	37.33 ± 7.82 d
Analyses of variance		F-values	F-values
pH		2.92 *	18.47 ***
MC		1.65	1.58
pH × MC		0.07	0.12

Manawatu potato trial Treatments		$Ca(NO_3)_2$-Cd (μg kg^{-1})	$Ca(NO_3)_2$-Zn (μg kg^{-1})
pH- 1	MC-0	17.09 ± 0.2 a	382.61 ± 20.73 b
	MC-25	13.73 ± 1.53 a	731.5 ± 109.45 a
	MC-50	9.91 ± 2.71 b	735.88 ± 96.22 a
pH- 2	MC-0	6.28 ± 1.32 c	110.95 ± 29.52 c
	MC-25	4.29 ± 1.08 cd	151.8 ± 50.44 c
pH- 3	MC-0	2.62 ± 1.22 cd	46.83 ± 9.78 c
	MC-25	2.26 ± 0.38 d	61.31 ± 11.01 c
pH- 4	MC-0	1.61 ± 0.42 d	30.26 ± 4.73 c
	MC-25	1.63 ± 0.61 d	47.58 ± 9.85 c
pH- 5	MC-0	1.20 ± 0.12 d	28.1 ± 2.24 c
Analyses of variance		F-values	F-values
pH		43.79 ***	63.28 ***
MC		8.16 **	8.56 **
pH × MC		0.82	5.21 **

Canterbury potato trial Treatments		$Ca(NO_3)_2$-Cd (μg kg^{-1})	$Ca(NO_3)_2$-Zn (μg kg^{-1})
pH- 1	MC-0	5.78 ± 0.44 a	145.31 ± 17.94 b
	MC-25	4.73 ± 0.82 ab	246.92 ± 64.16 a
	MC-50	4.31 ± 0.62 b	224.09 ± 14.76 a
pH- 2	MC-0	0.90 ± 0.18 c	13.77 ± 2.18 c
	MC-25	0.74 ± 0.1 c	19.72 ± 4.48 c
pH- 3	MC-0	0.56 ± 0.09 c	15.29 ± 1.42 c
	MC-25	0.51 ± 0.05 c	11.73 ± 0.81 c
pH- 4	MC-0	0.35 ± 0.08 c	11.02 ± 0.17 c
	MC-25	0.40 ± 0.04 c	12.54 ± 0.76 c
pH- 5	MC-0	0.30 ± 0.06 c	9.37 ± 0.67 c
Analyses of variance		F-values	F-values
pH		63.55 ***	26.36 ***
MC		18.35 ***	8.64 **
pH × MC		9.84 ***	18.32 ***

Canterbury wheat trial Treatments		$Ca(NO_3)_2$-Cd (μg kg^{-1})	$Ca(NO_3)_2$-Zn (μg kg^{-1})
pH- 1	MC-0	13.03 ± 2.67 a	255.42 ± 65.36 a
pH- 2	MC-0	11.85 ± 4.98 a	207.19 ± 101.39 a
	MC-25	3.89 ± 1.13 b	151.96 ± 25.72 ab
	MC-50	3.74 ± 0.94 b	226.59 ± 46.15 a
pH- 3	MC-0	4.05 ± 1.73 b	66.45 ± 29.7 bc
	MC-25	1.13 ± 0.24 b	18.58 ± 4.62 bc
pH- 4	MC-0	1.57 ± 0.54 b	30.53 ± 16 bc
	MC-25	0.41 ± 0.09 b	19.77 ± 5.10 bc
pH- 5	MC-0	1.07 ± 0.09 b	10.60 ± 3.21 c
	MC-25	0.89 ± 0.16 b	11.89 ± 3.41 c
Analyses of variance		F-values	F-values
pH		9.35 ***	11.45 ***
MC		4.01 *	0.82
pH × MC		1.6	0.21

Data in the table shows the means of three replicates ± standard error, and the same letters between treatments in each column represent for non-significance at the 5% level. Significance levels of lime, compost and the interaction Lime × compost are indicated: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

4.3.3 Effects of amendments addition on yield and uptake of Cd in plants

There was a significant difference in tuber Cd between the sites. The average Cd concentration in potato across all treatments in Canterbury was 0.13 mg kg^{-1}, which was significantly higher than that in Pukekohe (0.08 mg kg^{-1}, DW), while Manawatu had the lowest Cd concentration in potato (0.04 mg kg^{-1}) (Figure C5 in the Appendix). The overall average Cd concentration in grain was 0.08 mg kg^{-1} (DW) in the Canterbury wheat trial.

There were no significant liming-induced effects on tuber Cd concentration in the potato trials (Table 4.6). Similarly, the effect of compost on Cd uptake by potato tuber was only significant in the Manawatu trial. In Pukekohe, consistent with the reduction of $Ca(NO_3)_2$ extractable Cd concentration at higher pHs, the treatment combining the highest liming and 25 t ha^{-1} compost application had the lowest Cd concentration in potato tubers (Figure 4.1, A-1). The highest concentration of extractable Cd appeared in the treatment with the application of sulphur, and this treatment had the highest Cd concentration in potato tuber which was 29.9% higher than that in the non-amendment treatment. Likewise in Manawatu, the treatment with the highest Cd availability had the highest concentration of tuber Cd. In the Canterbury potato trial, however, the treatment combining the second lowest liming (pH-2) and 25 t ha^{-1} compost addition had the highest tuber Cd concentration at 0.143 mg kg^{-1}, but there were no significant differences of tuber Cd concentration between different treatments.

Liming and compost application significantly influenced Cd concentrations in wheat grain (Table 4.6). Briefly, compared with the treatment without amendments in the Canterbury wheat trial, the application of lime significantly increased the concentration of grain Cd (Figure 4.1, D-1). This is in contrast to expectations as higher lime addition is higher pH. When compared to the lowest pH treatments, the greatest increase in Cd concentration in wheat grain was observed in the treatment applying the largest rate of lime where wheat grain Cd concentration was significantly increased by 91.9%. At each level of liming, 25 t ha^{-1} compost addition reduced Cd uptake by plants, while a larger rate of application at 50 t ha^{-1} achieved a non-significant effect on Cd accumulation in wheat grain. The largest reduction of wheat grain Cd concentration (78.2%) in response to compost application was achieved at the third liming-rate (soil pH = 6.37) treatment. Amendment addition did not significantly affect the yield of potato and wheat in all field trials (Table C2 in Appendix). Due to a flooding in the Manawatu, the growth of potato seedlings in some plots was affected. Thus, the yield of potato in the Manawatu was not considered in this study.

Table 4.6 The effects of applied amendments on plant Cd and Zn concentrations in the four trials.

Species	Location	Analyses of variance	Plant Cd		Plant Zn	
			F-values	Significance	F-values	Significance
Potato	Pukekohe	pH	2.57	0.07	2.52	0.07
		MC	1.24	0.31	2.54	0.10
		pH × MC	0.18	0.91	0.88	0.47
	Manawatu	pH	0.60	0.66	0.90	0.48
		MC	6.43	< 0.01 **	0.32	0.73
		pH × MC	1.75	0.19	0.57	0.64
	Canterbury	pH	1.46	0.36	6.30	< 0.01 **
		MC	0.91	0.42	1.63	0.22
		pH × MC	0.72	0.55	0.85	0.49
Wheat	Canterbury	pH	6.23	< 0.01 **	1.43	0.26
		MC	12.58	< 0.001 ***	2.29	0.13
		pH × MC	1.36	0.29	0.15	0.93

Significance levels of lime, compost and the interaction Lime × compost are: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

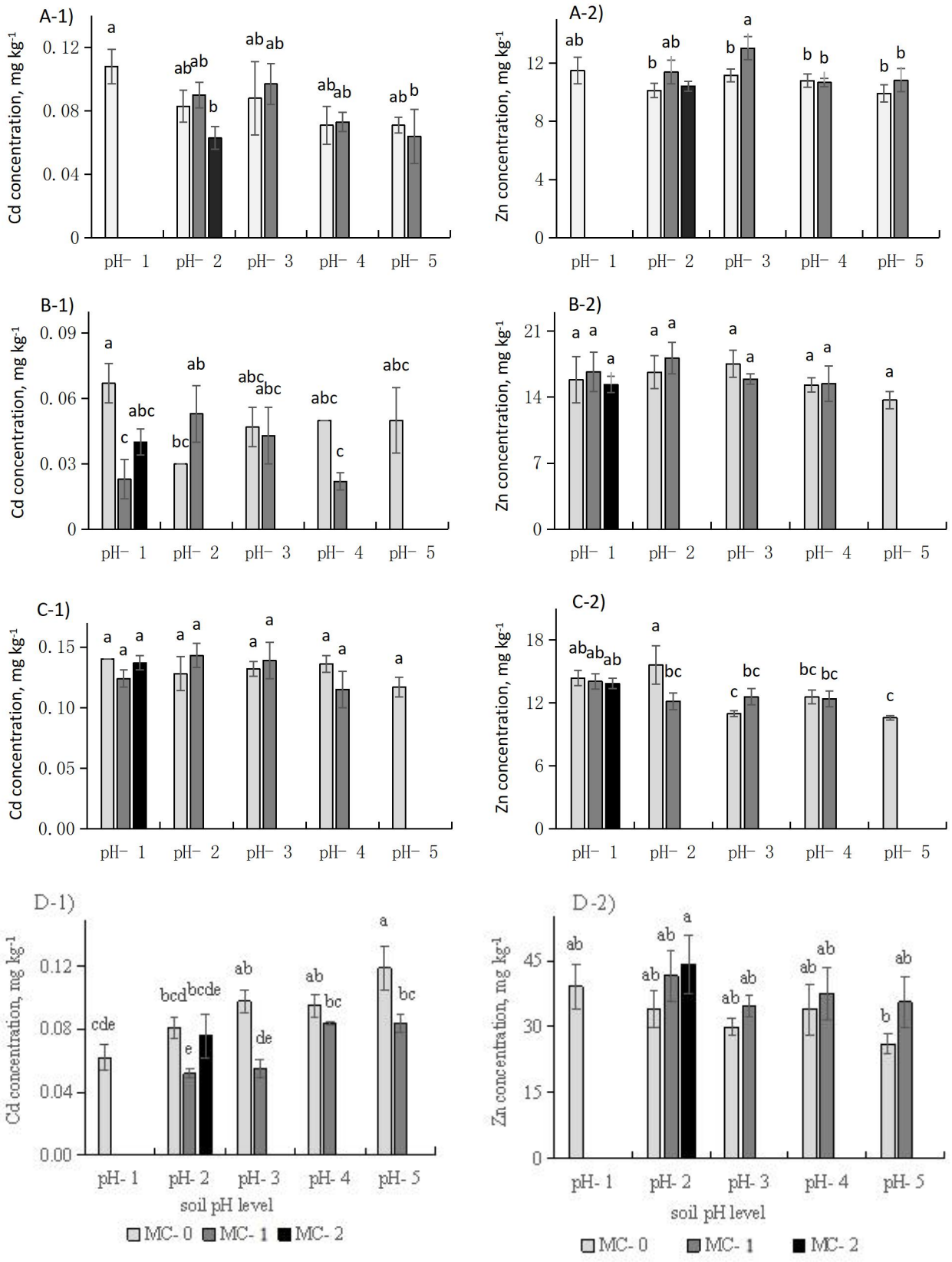

Figure 4.1 Cd (left) and Zn (right) concentrations (DW) in edible parts of (A-C) potato (A: Pukekohe trial; B: Manawatu; C: Canterbury) and (D) wheat. Letters above the bar diagram stand the difference at significance level $P < 0.05$ among different treatments.

4.4 Discussion

4.4.1 Effects of lime and compost addition on the bioavailability of soil Cd

The $Ca(NO_3)_2$ extraction representing the exchangeable form of metal has been used to estimate the bioavailable fraction of soil metals in many studies (Simmler et al., 2013; Valentinuzzi et al., 2015). Within un-amended treatments the soil extractable Cd, on average, consisted of 5.0 %, 10.1 %, 11.8 % and 4.0 % of the soil total Cd concentration in the Pukekohe potato, Manawatu potato, Canterbury wheat, and Canterbury potato trials respectively. These proportions of soil Cd in exchangeable form are similar to reports (0.7 – 6.0 %) by Gray et al. (1999a) and Gray et al. (1999b), but slightly lower than those in Salmanzadeh et al. (2016) which showed that in some volcanic soils, up to 15% of the total Cd was exchangeable. In Pukekohe, the reduction of exchangeable Cd by liming was negligible, but sulphur addition increased $Ca(NO_3)_2$ extractable Cd. The lower sensitivity to pH in the volcanic soils from the Pukekohe area was also observed by Al Mamun et al. (2016). They showed that the values of the Cd adsorption coefficient (K_d) in a volcanic soil did not respond as strongly (increase) to increasing pH than in non-volcanic soils. This is likely because volcanic soils can have greater amounts of negative charge due to higher soil organic carbon contents and larger abundance of allophane (a hydrous aluminium silicate clay mineraloid with amorphous/poorly crystalline structure), which can buffer additional modifications induced by amendments (Bolan et al., 2003a). The sharp decline of extractable Cd with increasing soil pH is consistent with other reports (Al Mamun et al., 2016; Al Mamun et al., 2017; Benyas et al., 2018; Bolan et al., 2003b), indicating that soil pH is a dominant environment factor in determining Cd bioavailability. This might be explained by that liming transferred the solid phases of Cd from exchangeable fractions to less bioavailable forms in moderately acidic soils (Al Mamun et al., 2017; Benyas et al., 2018; Bolan et al., 2003b; Gray et al., 1999c; Valentinuzzi et al., 2015).

Compost additions generally raised soil pH in acidic and neutral soils although this effect was only statistically significant at the Manawatu site. The possible explanations for the increase of pH might be due to the mineralization of C, OH^- ion released by ligand exchange and the introduction of basic cations (Tlustos et al., 2006). Also, the pH of compost used was 7.2, which could contribute to raising the soil pH (Table 4.2). The soil carbon and Zn concentrations (Table C1 in Appendix) were raised in most field trials ($P < 0.05$), in line with other studies which indicated the effects of compost application on soil properties (Al Mamun et al., 2016; Khan et al., 2017). Compost application significantly affected the bioavailability of soil Cd. The reduction of $Ca(NO_3)_2$ extractable Cd due to compost addition is in agreement with findings in other studies (Al Mamun et al., 2017; Khan et al., 2017; Loganathan et al., 2012). This may be because the compost application increases soil

concentrations of the functional groups, such as carboxyl (–COOH), phenolic (Ph–OH) and sulfhydryl (–SH) groups, which may enhance Cd binding to colloids and subsequently decrease its extractable proportions through cation exchange and translocation of metals to stable organometallic complexes (Loganathan et al., 2012; Six & Smolders, 2014). Consistent with the effects of liming, the different responses of soil $Ca(NO_3)_2$ extractable Cd to compost addition between trials coincide with other studies (Khan et al., 2017; Mbarki et al., 2008) indicating an essential role of soil types in soil Cd remediation. Also, the power of compost in reducing Cd availability decreased with an increase in pH. Compared to the no compost treatments at the different liming rates, the addition of 25 t ha^{-1} of compost Canterbury wheat trial lowered the $Ca(NO_3)_2$ extractable Cd concentrations from 7.96 to 0.18 µg kg^{-1} as the liming rate increased. Similar results have been reported by (Simmler et al., 2013) where lignite application appeared to be more effective in reducing exchangeable Cd at low pHs. The reduction of Cd immobilised with increasing pH might be explained by the increase of dissolution of humic acids at high pH, which increases the availability of soil Cd by forming soluble organic complexes.

4.4.2 Effects of lime and compost application on Cd accumulation in plants

Soil pH amendment did not achieve significant reductions of Cd concentration in tubers in the potato trials. In contrast, Cd accumulation in wheat grain was enhanced significantly after the lime application (Table 4.6). This is supported by a correlation analysis indicating a significant negative relationship (between soil $Ca(NO_3)_2$ extractable Cd concentration and soil pH (R = -0.95, P < 0.01), but a poor relationship between plant Cd concentration and soil pH (R = - 0.05, P = 0.89; Manawatu potato trial in Table 4.7). The discrepancy between soil exchangeable Cd and plant Cd in response to liming has also been reported by others (Benyas et al., 2018; Jönsson & Asp, 2013; Yang et al., 2018). Bolan et al. (2003b) found the lime-borne Ca^{2+} competed for adsorption sites and increased the concentration of Cd^{2+} in soil solution at high pH soils where lime had been added, and consequently enhanced plant Cd accumulation. In some circumstances, increasing soil pH can increase nutrient availability, alleviate Al & Mn toxicity, and improve plant health state, which promotes Cd uptake by plants (Wang et al., 2006a). Additionally, the negative correlation between soil pH and soil exchangeable Zn concentration indicated that liming also significantly reduced the bioavailability of soil Zn, an essential micronutrient for plants. This is also confirmed by a more than 30% of decline induced by liming in wheat grain Zn concentration when compare plant Zn concentration in the treatment with the largest liming rate to the lowest one in Canterbury wheat trial. Similarly, potato Zn concentration was significantly reduced by the application of lime in the Canterbury potato trial (Table 4.6). Potato Zn concentration was significantly reduced when the soil pH was raised to 6.79

(Figure 4.1, D-1). Liming-induced Zn deficiency in the rhizosphere may enhance the relative genes (*OsNramp5* and *OsIRT1*) expression, which enhances Cd uptake capacity by the root (Yang et al., 2018).

Table 4.7 Pearson correlation coefficients of the relationships between plant Cd & Zn concentration and soil parameters.

Soil parameter	$Ca(NO_3)_2$ extractable metals (mg kg^{-1})		Plant metals (mg kg^{-1} DW)		$Ca(NO_3)_2$ extractable metals (mg kg^{-1})		Plant metals (mg kg^{-1} DW)	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn
	Pukekohe potato trial				Manawatu potato trial			
pH	- 0.47 **	- 0.78 ***	- 0.38 *	- 0.06	- 0.95 ***	- 0.80 ***	- 0.05	- 0.17
Total C (%)	0.02	0.08	0.09	- 0.24	0.05	0.55 **	- 0.57 **	- 0.11
Total N (%)	0.27	- 0.18	- 0.47 ***	0.21	- 0.03	0.41 *	- 0.30	- 0.10
Total Cd (mg kg^{-1})	0.44 *	0.42 *	0.23	0.15	- 0.01	- 0.11	- 0.11	0.13
Total Zn (mg kg^{-1})	- 0.31	0.15	0.28	-0.40 *	- 0.05	0.36 *	- 0.22	0.17
Total Ca (mg kg^{-1})	- 0.39 *	- 0.76 ***	- 0.39 *	- 0.04	- 0.49 **	- 0.38 *	- 0.26	- 0.33 *
CEC	- 0.22	- 0.41 *	- 0.15	0.18	0.25	0.27	- 0.26	- 0.37 *
$Ca(NO_3)_2$ - Cd (μg kg^{-1})		0.58 ***	0.16	0.22		0.70 ***	0.14	0.24
$Ca(NO_3)_2$ - Zn (μ kg^{-1})			0.31	0.12			- 0.30	0.02
plant Zn (mg kg^{-1})			0.16				0.19	
	Canterbury potato trial				Canterbury wheat trial			
pH	- 0.95 ***	- 0.87 ***	- 0.12	- 0.64 ***	- 0.71 ***	- 0.76 ***	0.27	- 0.29
Total C (%)	- 0.20	0	- 0.20	0.15	- 0.22	0.08	- 0.01	0.72 ***
Total N (%)	0.19	0.22	0.05	0.38 *	- 0.29	- 0.10	- 0.10	0.21
Total Cd (mg kg^{-1})	0.07	0.05	0.34	0.15	- 0.08	- 0.17	- 0.05	0.11
Total Zn (mg kg^{-1})	0.30	0.44 *	- 0.13	0.27	- 0.23	0.07	- 0.06	0.62 ***
Total Ca (mg kg^{-1})	- 0.54 **	- 0.48 **	- 0.19	- 0.45 *	- 0.57 **	- 0.62 ***	0.43 *	- 0.25
CEC	0.37 *	0.26	0.20	0.12	- 0.67 ***	- 0.68 ***	0.34	- 0.11
$Ca(NO_3)_2$ - Cd (μg kg^{-1})		0.91 ***	0.06	0.57 ***		0.87 ***	- 0.23	0.17
$Ca(NO_3)_2$ – Zn (μg kg^{-1})			0.00	0.59 ***			- 0.30	0.42 *
plant Zn (mg kg^{-1})			0.38 *				- 0.11	

Significance levels are indicated as: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

In the Manawatu trial, 25 t ha^{-1} compost application significantly decreased potato tuber Cd concentration when no lime was applied (Figure 4.1, B-1). However, compost addition in this study did not significantly influence on the Cd uptake by potato in other two trials. This is in contrast with the findings from a pot experiment (Al Mamun et al., 2017) where amending the soil with 75 t ha^{-1} of green waste compost raised soil C content by 77% from 2.29 % and subsequently contributed to a significant reduction of both $Ca(NO_3)_2$-extractable and potato tuber Cd concentration. In the current study, applying the same compost at the rate of 50 t ha^{-1} only increased soil total C by 1.4 - 24.4% in different trials. The non-significant effect of composting may be because the composting-induced changes of soil organic carbon in the field trials were not big enough to make a difference on the capacity of soils in binding soil Cd at each field trial. The observed non-significant correlation between soil C and concentrations of $Ca(NO_3)_2$ extractable Cd is consistent with this rationale (Table 4.7). The application of compost significantly reduced the wheat grain Cd concentration, but increased grain Zn. Coinciding with the changes of soil Zn after compost application, the

concentration of grain Cd was significantly correlated with soil C content. The contrasting response of grain Cd and grain Zn to the addition of compost indicated that composting may alleviate lime-induced Zn deficiency and reduce Cd accumulation in grain. Compost was more consistent in the reductions of plant Cd concentration than lime which may be partly due to the presence of soft Lewis bases (e.g. –SH groups) in compost which bond Cd^{2+} more strongly than the intermediate Lewis acid, Zn^{2+} (Alloway, 1990; Welikala et al., 2018).

4.4.3 Effects of the trial location on Cd accumulation in plants

In this study, there is no single soil variable that correlates significantly with plant Cd concentration across trials (Table 4.7). This is similar to the findings by McLaughlin et al. (1997), who reported that potato Cd concentrations did not significantly correlate to soil pH, DOC and the Cd concentration in EDTA, $CaCl_2$ and $Ca(NO_3)_2$ extractions. The lowest Cd concentration in potato tuber was observed at 0.115 mg kg^{-1} in the Canterbury potato trial which combined the second highest liming (pH 4) and 25 t ha^{-1} compost addition, which was higher than those in all the treatments of other trials. This implies that region (the location of trial) may play an important role in Cd concentration in potato tuber. It is confirmed in a three-way ANOVA analysis showing that location significantly affected Cd enrichment in potato tubers ($P < 0.001$) (Table 4.8). The location effects may be attributable to environmental factors contributing to the differences in climate and soil variables. The potatoes grown in the Canterbury trial had a higher Cd concentration, in line with the results from our national survey (Chapter 8). The sedimentary soil in the Canterbury trial tends to have a larger Cd transfer coefficient from soil to plant as shown in a previous study (Cavanagh et al., 2016). A higher Cd concentration in potato in the Canterbury trial may likely be also due to its lower rainfall (Table 4.1). A more frequent irrigation results in more temporary fluctuations in soil moisture content, which can increase soil Cd bioavailability (Stafford et al., 2018a). Similar significant effects of location on Cd accumulation were also found for onions, lettuces and pasture forage (Cavanagh et al., 2016). Due to the variation of Cd in plants between experimental sites, Cavanagh et al. (2019) highlighted the potential risk of only using soil properties as indicative factors to assess Cd uptake by plants.

Table 4.8 The effects of environmental factors on Cd and Zn concentrations in potatoes.

Analyses of variance	plant Cd		plant Zn	
	F-values	Significance	F-values	Significance
pH	2.62	0.04 *	8.06	< 0.001 ***
MC	6.35	< 0.01 **	0.44	0.65
Location	180.73	< 0.001 ***	47.10	< 0.001 ***
pH × MC	1.86	0.12	0.61	0.69
pH × Location	0.59	0.78	1.07	0.40
MC × Location	1.53	0.22	1.17	0.33
pH × MC × Location	0.21	0.96	1.09	0.38

Significance levels of lime, compost and the interaction Lime × compost are indicated: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

4.5 Conclusion

In this study, the potential of lime and compost for minimising plant uptake of Cd was evaluated in NZ cropping systems under field conditions. Results from the field trials indicate that the application of lime and compost affected the concentration of soil $Ca(NO_3)_2$ extractable Cd significantly. However, their effects on plant Cd concentration varied between sites. There also was no significant interaction between lime and compost addition on soil Cd concentration in $Ca(NO_3)_2$ extracts and plants. The discrepancy between soil extractable Cd and plant Cd concentration in response to soil amendments indicates a limitation of the $Ca(NO_3)_2$ extraction's ability to predict Cd uptake by plant. Potatoes grown in Canterbury had the highest Cd concentration in the tubers, compared to those grown in Pukekohe and Manawatu. The induced changes of soil pH and organic C by amendments addition did not cause significant effects on Cd uptake by potatoes. Lime addition can induce a significant decline of Zn concentration in potatoes in the Canterbury potato trial. In the wheat trial, liming significantly increased Cd concentrations in wheat grain, while compost addition increased soil Zn concentration, which might buffer lime-induced Zn deficiency and reduce Cd uptake by wheat. With the aim to test effects of pH changes on Cd accumulation in plants, artificially high rates of lime application raised soil pH to around 7.0 (7.2 in Pukekohe) in this study, which are higher than typical application rates. However, the increase of wheat Cd concentrations in the Canterbury highlights the risk of using lime for minimising Cd accumulation in wheat grown at this area.

Chapter 5

Cadmium accumulation in New Zealand agricultural soils: a prediction for the next 25 years

A manuscript from this chapter has been prepared for submission to the *Science of the Total Environment*.

My contribution to this article: I collated the data, run a model and developed the original draft of the manuscript with the help of my co-authers.

5.1 Introduction

Intense industrialization, expanding population and accelerated urbanization in the last few decades have contributed to a lowering global environmental quality. Amongst the worldwide environmental issues, soil contamination associated with cadmium (Cd), both diffuse and localised, has raised concerns on food security, the related potential health risks and the detrimental effects on soil ecosystems. Occurring as a non-essential trace element for both plants and animals, Cd can accumulate in the human body and cause many negative health impact after chronic exposure. In the worldwide surface environment, the anthropogenic sources of soil Cd include mining, waste disposal, vehicle exhausts, fertiliser application and so on (Alloway et al., 1990; Loganathan et al., 2012). Upon entering the soil it can accumulate to levels where crops produced from those soils may cause food safety problems for consumers (He & Singh, 1994; Jiao et al., 2012; McLaughlin & Singh, 1999).

Most Cd in foods originates from the soils where animals are raised and crops are grown. Soil Cd concentration can be a major factor determining the amount of Cd taken up by plants, although other factors, such as soil variables (Cavanagh et al., 2016; Gray et al., 1999a), plant species and cultivars (Ashrafzadeh et al., 2017; Cavanagh et al., 2016; Gray et al., 2001) and soil management practices (Cooper et al., 2011; Gray et al., 2006) can also be important. When soil Cd concentrations increase, there can be an associated risk of elevated levels of plant Cd when other environmental factors are constant (Six & Smolders, 2014). Managing the soil Cd mass balance to prevent excessive accumulation in crops is a fundamental strategy to manage the risk of dietary exposure to Cd. Hence, limits of Cd concentration in soils used for agricultural purposes have been proposed. In the

Netherlands, the maximum permissible addition (MPA) of Cd concentration was established at 0.76 mg kg^{-1} by dividing the maximum Cd concentration which poses no significant influence on the tested organisms by ten (Crommentuijn & Polder, 1997). Based on the soil background levels, the maximum guideline value ('target' threshold) was set at 0.8 mg kg^{-1}. Similarly, in some other countries, permissible Cd concentrations in agricultural soils have also been introduced, such as 0.4 mg kg^{-1} in Japan (rice land) (Makino et al., 2016), 0.3 mg kg^{-1} in Southern China (dry land) (Zhao et al., 2014), 0.8 mg kg^{-1} in Northern China (dry land) (Ji et al., 2012), 0.4 mg kg^{-1} in Taiwan, China (Römkens et al., 2009) and 3.0 - 6.0 mg kg^{-1} in India (Bhatti et al., 2016), where soils with Cd concentrations higher than these maximum permissible thresholds should be phased out of agricultural purposes or replaced by non-food crops. In New Zealand (NZ), there are no specific permissible soil Cd concentrations in cropping and pastoral farming systems. The TFMS recommends that farms which have soil Cd concentrations > 0.6 mg kg^{-1} should also use annual superphosphate up to 45 kg P ha^{-1}, or switch to lower Cd concentration phosphorus (P) fertilisers, such as phosphoric acid derived and nitric acid derived P products (Sneath, 2015). The phosphoric acid and nitric acid derived products are generally more expensive, which may increase farmers' cost.

Cd accumulation in soils occurs when Cd inputs exceed its losses. The main sources of Cd inputs in agricultural systems include: atmospheric deposition (Gray et al., 2003a), fertiliser application (McDowell et al., 2013; Taylor, 1997), biosolids (McLaren et al., 2004) and animal feeds and manure application (Roberts & Longhurst, 2002; Sheppard et al., 2009). The main loss pathways for soil Cd include: plant uptake (Stafford et al., 2016), animal soil digest (Lee et al., 1996; Reiser et al., 2014), leaching and outwash (Gray et al., 2003b; Gray et al., 2017c; McDowell, 2010; McDowell, 2012) and soil erosion (Quinton & Catt, 2007). Based on the mass balance in agricultural systems, various international models have been developed to predict Cd accumulation in some countries, such as Australia (de Vries & McLaughlin, 2013), the European Union (Six & Smolders, 2014) and Canada (Sheppard et al., 2009) (Table D1 in Appendix). The uncertainties in these models are determined by Cd inputs which are mainly affected by the P fertiliser application rate and Cd concentration in P fertilisers, as well as Cd outputs which are mainly composed of Cd loss via plants uptake and leaching. In NZ, the various soil properties, climatic conditions and fertiliser management practices in farming systems of different regions, have contributed to the variation of soil Cd distribution in NZ agricultural systems (Reiser et al., 2014; Stafford et al., 2018b). The Cd balance in NZ agricultural soils was simulated in this study by employing the mass-balance model developed by Six and Smolders (2014). This model considered the influence of soil variables, such as pH and soil organic carbon (OC), as well as climatic factors on soil Cd accumulation. Moreover, this model was the only

one that applied a sensitivity analysis with Monte Carlo simulation to identify the variability in soil Cd trends, which was taken into consideration in this study.

In NZ, a mass-balance model ("CadBal" model) was developed to assess the possible risks associated with fertiliser-derived Cd. CadBal estimates temporal changes in soil Cd concentrations by considering Cd inputs from atmospheric deposition, fertiliser and biosolids application, as well as Cd losses from leaching, soil erosion and crop offtake. The model also includes factors such as types of agricultural land use and soil parameters (bulk density and depth) and has been tested for five of NZ's 15 soil orders (*Allophanic, Brown, Pumice, Pallic* and *Organic*) (Gray & McDowell, 2016; Gray et al., 2003b). It has been used to simulate Cd accumulation in soils collected from a long-term NZ field trial (McDowell, 2012; Roberts & Longhurst, 2005), and estimate possible Cd accumulation in the future (McDowell, 2012; Salmanzadeh et al., 2017a; Taylor et al., 2007). However, there are some limitations to its application, many of which were identified by Taylor et al. (2007). Arguably, the most important limitations are that (1) the losses of Cd through leaching are not linked to localized climatic conditions and (2) important soil characteristics for determining a soil's capacity to retain Cd are not specifically considered, instead, the model has been calibrated against specific soils belonging to the different soil orders. These constrain the accuracy of the model to specific soils and the latter is especially important as it does not allow CadBal to account for highly variable factors of different soils/land-uses.

The CadBal model relies on deterministic principles and, hence, cannot be used extensively to test the uncertainty in predicted soil Cd accumulation arising from the natural variation associated with environmental variables such as the accumulation of soil organic matter under pasture (Cadmium Working Group, 2008) and changes in soil pH arising from farm management practices. On the other hand, stochastic models allow for a greater variety of variables (Waller et al., 2003). The major advantage of using a stochastic model is that it makes uncertainty explicit by providing insights into a range of possible modelling outcomes including the sensitivity of those outcomes (Ponciano et al., 2005). Keller et al. (2001) used a stochastic model to simulate the effects of site-specific soil properties and non-site specific fertiliser management practices on P, Cd and Zn fluxes for agricultural soils in Switzerland, and showed a good agreement between the modelled and measured soil P, Cd and Zn concentrations. Peng et al. (2016) applied a stochastic Cd mass balance model to evaluate the efficacy of soil Cd remediation strategies, and found that not returning rice straw to paddy soils could reduce soil Cd accumulation effectively. Similar successful applications of stochastic balance models to simulate variables with statistical consideration of the system-wide variability have also been widely used to model random processes in other scientific research

(Costello et al., 2005; Lande et al., 2003; Toni & Stumpf, 2009). Monte Carlo simulation (or probability simulation) is a technique used to identify risks and uncertainties in forecasting models (Binder et al., 1993). Chen et al. (2007) applied a stochastic model in a Monte Carlo framework to estimate the possibility of soil Cd concentrations exceeding the maximum permissible limit with the long-term application of Cd-containing P fertilisers. To date, such uncertainty-based risk assessments have not been applied to predicting soil Cd accumulation in NZ, and as such, the variability inherent to NZ soils and their management in agriculture, or the climatic variability on regional scales, have not been considered. Consequently, the confidence in the previous model predictions of Cd accumulation has not been systematically examined. Hence, in this study, a modelling exercise was undertaken to carry out a probabilistic risk-based assessment of future Cd accumulation in NZ agricultural soils. The model of Six and Smolders (2014) was extended to consider the uncertainty of a larger number of input parameters in a Monte Carlo framework (forthwith this will be referred to as the stochastic cadmium model, "SCM"). The aim of this study was to provide a future perspective of possible changes in the distribution of Cd concentrations under different soil and land use combinations subject to different management practices. This study was sought to elucidate the effects of soil types, farming purposes, irrigation levels, P application rate and Cd concentration in fertiliser on soil Cd accumulation. A risk assessment of soil Cd concentration exceeding the maximum designated value (assumed at 1.0 mg kg^{-1} in this study) and its possible implications to farmers in different farming systems and regions of New Zealand would be useful for the development of soil Cd management policies and fertiliser application guidelines.

5.2 The model (SCM) description

Cd accumulation in the SCM was calculated from the annual difference between input and removal as shown in Equation (Eq.) 2.

$$Cd_{s,t} = Cd_{s,t-1} + (Cd_{in} - Cd_{out}) / 10\rho d \qquad \text{Eq. (2)}$$

Where $Cd_{s,t}$ is the concentration of soil Cd (Cd_s, mg kg^{-1}) at time t, while Cd_{in} and Cd_{out} are annual total input and total loss of soil Cd and they are expressed as g ha^{-1} yr^{-1}; bulk density (ρ) is expressed as kg m^{-3}; soil depth (d) is expressed as m; and Cd is assumed to be evenly distributed within the modelled soil depth (7.5 or 10 cm, see below).

5.2.1 Cadmium Inputs to soil

As mentioned above, Cd sources in NZ mainly include atmospheric deposition and fertiliser application. However, although sludge application is considered as a Cd source, it is not normally

applied to all agricultural lands in NZ and was not considered in the model. The Cd input is calculated as:

$$Cd_{in} = Cd_{ad} + R \times Cd_{fert} \quad \text{Eq. (3)}$$

Where Cd_{ad} is the annual atmospheric deposition of Cd (g ha^{-1}). R is the annual rate of P fertiliser usage (kg ha^{-1}) and Cd_{fert} is the Cd concentration in P fertiliser (mg kg^{-1}).

5.2.2 Cadmium losses from soil

The removal of Cd from the top soils include Cd plant uptake ($Cd_{plant\ -\ offtake}$), leaching losses into deeper horizons (Cd_{leach}), surface runoff (Cd_{wash}) and soil erosion. New Zealand has high rates of soil erosion. Around 7% of land in the North Island has a high risk of soil erosion, especially the Gisborne Region (Statistics New Zealand, 2018). However, due to a lack of available data, the effects of erosion (including Cd_{wash}) on Cd accumulation were not considered in this study.

Crop offtake

In cropping soils, where crop offtake ($Cd_{crop\ -\ offtake}$) was determined by annual plant biomass (Y, kg ha^{-1}) and the concentration in plants (Cd_{plant}, mg kg^{-1}) (Eq. 4) (Six & Smolders, 2014). The Cd concentration in crops ($Cd_{plant\ -\ crop}$) was estimated using a soil-to-plant transfer factor (T_{fs}, Eq. 5).

$$Cd_{crop\ -\ offtake} = Y \times Cd_{plant\ -\ crop} \quad \text{Eq. (4)}$$

$$Cd_{plant\ -\ crops} = Cd_{s} \times T_{fs} \quad \text{Eq. (5)}$$

The T_{fs} was calculated as the ratio of Cd concentrations between the plant (DW) and soil (Cd_{plant}/Cd_{s}). T_{fs} values for different soil types for common crops in NZ are shown in Table 5.1a & b.

Most Cd removal from pastoral systems is through pasture offtake ($Cd_{pasture\ -\ offtake}$), and the contribution of soil ingestion is negligible (Sheppard et al., 2009). Lee et al. (1996) reported that most of the daily intake of Cd by animal grazing was returned to the soil through faeces, while <1% of Cd was removed via accumulated in the body. Hence, in this study, 1% of Cd uptake by pasture was assumed to accumulate into animal products or be transferred to non-productive parts of the farms. Hence, the Cd uptake by pasture was estimated according to Eq. 6 and Eq. 7

$$Cd_{pasture\ -\ offtake} = Y \times Cd_{plant\ -\ pasture} \times 0.01 \quad \text{Eq. (6)}$$

$Cd_{plant\ -\ pasture} = Cd_s \times T_{fs}$ Eq. (7)

Table 5.1 a) Cadmium soil-plant transfer factors (T_{fs}) for perennial ryegrass in agricultural soils according to soil orders. b) Cadmium soil-plant transfer factors (T_{fs}) for various forage and crop plants in NZ.

a)

Soil order	Soil Cd (mg kg^{-1})	Cd in Ryegrass (mg kg^{-1}, DW)	Transfer factors (T_{fs})	Reference
Organic	0.15	0.05	0.38	(Gray & McDowell, 2016)
Pumice	0.45	0.16	0.36	(Gray et al., 1999a)
Sedimentary [a]	0.15	0.14	1.29	(Gray et al., 1999a)
	0.19	0.20	1.04	(Gray et al., 1999c)
	0.53	0.29	0.54	(Simmler et al., 2013)
	0.43	0.10	0.24	(Stafford et al., 2016)
	1.31	0.55	0.42	(Benyas et al., 2018)
Mean	*0.52*	*0.25*	*0.70*	
Volcanic [a]	1.04	0.29	0.30	(Gray et al., 1999a)
	1.06	0.35	0.40	(Gray et al., 1999c)
Mean	*1.05*	*0.32*	*0.35*	
Others [a]	0.15	0.15	1.07	(Gray et al., 1999a)
	3.20	0.59	0.19	(Gray & McLaren, 2005)
Mean	*1.67*	*0.37*	*0.63*	

Note: [a] For Sedimentary, Volcanic and Others soils, the mean value of T_{fs} was used for models; each number in this table was the mean value calculated from its corresponding study if there were more than one values.

b)

Plants	Transfer factors (T_{fs})	Reference	Plants	Transfer factors (T_{fs})	Reference
Herbage					
Ryegrass	0.92	(Gray et al., 1999a)	Clover	0.67	(Gray et al., 1999a)
	0.75	(Gray et al., 1999c)		0.62	(Gray et al., 1999c)
	0.19	(Gray & McLaren, 2005)		0.34	(Wakelin et al., 2016)
	0.41	(Simmler et al., 2013)		0.08	(Stafford et al., 2016)
	0.38	(Gray & McDowell, 2016)		0.12	(Cavanagh et al., 2016)
	0.22	(Stafford et al., 2016)		0.11	(Benyas et al., 2018)
	0.26	(Cavanagh et al., 2016)	*Mean*	*0.32*	
	0.35	(Benyas et al., 2018)			
Mean	*0.43*				
Plantain	1.61	(Stafford et al., 2016)	Chicory	3.59	(Stafford et al., 2016)
	1.31	(Cavanagh et al., 2016)		1.76	(Cavanagh et al., 2016)
	0.72	(Stafford et al., 2018a)	*Mean*	*2.68*	
Mean	*1.22*				
Crops					
Potato	1.26	(Cavanagh et al., 2016)	Wheat	0.34	(Gray et al., 1999a)
	2.39	(Ashrafzadeh et al., 2017)		0.73	(Gray et al., 1999c)
	0.01	(Al Mamun et al., 2017)		0.28	(Gray et al., 2001)
Mean	*1.22*			0.55	(Gray et al., 2002)
Onion	0.26	(Al Mamun et al., 2016)		0.33	(Cavanagh et al., 2016)
	0.17	(Cavanagh et al., 2016)	*Mean*	*0.45*	
Mean	*0.22*				

Note: The values of mean soil and plant Cd concentration were calculated by the concentrations in each study and T_{fs} values represent Cd_{plant}: Cd_{soil} ratio; each number in this table was the mean value calculated from its corresponding study if there was more than one value.

Leaching

Leaching losses were estimated using water flux and the Cd concentration in soil pore water (Eq. 8) (Six & Smolders, 2014):

$$Cd_{leach} = 10000 \times (F + I) \times Cd_{sol} \quad \text{Eq. (8)}$$

Where Cd_{sol} is the dissolved Cd concentration in pore water (or soil solution) (mg L^{-1}). F is annual precipitation excess (m yr^{-1}) and I is the annual volume of irrigation (m yr^{-1}). The pore water concentration was assumed to change proportional to soil total Cd (Cd_s), as determined by the soil/water partitioning coefficient (K_d; Eq. 9):

$$Cd_{sol} = Cd_s / K_d \quad \text{Eq. (9)}$$

As the variability of Cd concentrations in NZ agricultural soils is low, which is similar to Cd in European soils, the parameters for calculating K_d are those presented in Six and Smolders (2014) (Eq. 10).

$$\text{Log } K_d = -0.94 + 0.51 \times pH + 0.79 \log OC \quad \text{Eq. (10)}$$

Where *OC* is the soil organic carbon content (%).

To address the variability in climate conditions, daily weather data were collected in the four main regions from 2003 to 2017 (Table D2 in Appendix). Five climatic stations evenly located in the agricultural lands in Waikato and Canterbury were selected to represent the overall region, while three in the Bay of Plenty and Southland were selected due to their smaller agricultural area. In each region, the daily climatic data including rainfall (*R*), surface run-off (*S*) and evaporation (*E*) were taken into account. The weekly precipitation excess (F_{week}) was calculated using Equation 11.

$$F_{week} = R_{week} - S_{week} - E_{week} \quad \text{Eq. (11)}$$

Where F_{week} is the difference between daily *R*, *S* and *E*. Then the yearly precipitation excess was

$$F_{year} = F_{week1} + F_{week2} + \cdots + F_{week\ 52} \quad \text{Eq. (12)}$$

Where values of F_{week} were set to 0 if negative, which means no available precipitation excess.

5.3 Model validation

The assessment of the SCM was conducted based on soil monitoring results from the Winchmore Research Station, which is located in Canterbury, South Island of New Zealand (43°47′ S; 171°48′ E). The soil is the Lismore stony silt loam, belonging to the Orthic Brown soil order, according to the New Zealand soil classification system (Hewitt, 2010). The average annual rainfall at this site was 745mm (Smith et al., 2012). The trials at this station were set up in the 1950s to investigate the effects of different levels of superphosphate (SSP) fertiliser application (the "fertiliser trial") and irrigation (the "irrigation trial") on pasture production in a sheep grazing pasture system. The irrigation trial had three irrigation treatments: no irrigation and two with different irrigation rates. In the latter, irrigation was applied until the moisture contents in the top 10 cm soil reached 10 and 20% (w/w) for each treatment respectively. In this trial, all treatments had the same P application rate of 22 kg P ha^{-1} y^{-1}. The fertiliser trial received three rates of P fertiliser, including 0, 17 and 34 kg P ha^{-1} y^{-1}. For all the treatments, soils were irrigated at the same frequency to maintain soil moisture higher than 15% (top 10 cm soil). The full details of these two trials have been described in Rickard

and Moss (2012). Changes in soil Cd concentrations over time have been reported by Gray et al. (1999b); Kelliher et al. (2017) and McDowell (2012). CadBal has been applied for this site to predict the concentration of soil Cd over time (McDowell, 2012; Salmanzadeh et al., 2017a). The Cd accumulation by that model was compared to the accumulation predicted by SCM.

In this study, following the suggestions from Salmanzadeh et al. (2017a) on the application of CadBal in the Winchmore trials, the Cd concentrations in the P fertiliser in the year of 1998 were obtained from McDowell (2012), while the Cd concentrations from 1999 to 2030 were taken from Salmanzadeh et al. (2017a). However, soil bulk density measurements in the Winchmore trial have not been made over time. Schipper et al. (2013) indicated no significant differences of bulk density between irrigated treatments, so it was assumed that the average of topsoil bulk densities in the trials were 1.16 g cm^{-3} from 1952 to 1975, 1.07 g cm^{-3} from 1976 to 2005, and 0.91 g cm^{-3} from 2006 to 2030 (Gray et al., 1999b; Kelliher et al., 2017; McDowell, 2010). Different from the dryland treatment, the fertiliser trial is irrigated on average 4.3 times per year (0.1 m a time) to keep soil moisture higher than 15% (w/w) from 1952. Based on the average frequency and timing of irrigation, it was assumed that the same irrigation rate took place on the first day of every January, February, November and December, as well as 0.03 m on the first day of March (Srinivasan & McDowell, 2009). Also, because the fertiliser trial was flood irrigated, an average of 25% of the irrigation was estimated to be lost via surface runoff (McDowell & Rowley, 2008). The climatic data in the Winchmore trial between 1952 and 2017 was collected from a nearby weather station (Agent number, 4764, NIWA/AgResearch) and precipitation excess was calculated using equations 11 and 12. Consistent with CadBal, Cd lost via surface outwash was not included in the SCM. The data sets of modelling input parameters in previous studies and this study are shown in Table D3 and Table D4 in the Appendix.

5.4 Implementation and running SCM

In this study, the soil variables for SCM include soil Cd, soil organic carbon and soil bulk density. Soil Cd concentrations in NZ were obtained from Cavanagh (2014), which covered soil Cd information provided by regional councils, fertiliser companies, and research organisations. The information on soil properties (soil pH, total C content, and soil bulk density) was collated from a national environmental report (Ministry for the Environment of New Zealand, 2017). The soil-order classification followed the method used by the NZ fertiliser industry (Hewitt, 2010; Roberts & Morton, 2012). These data were used to derive appropriate probability distribution for the modelling inputs of the Monte Carlo simulations. The probability distributions fitting was performed

using the R package *fitdistplus* (Delignette-Muller & Dutang, 2015). The Akaike Information Criterion (AIC) was used to assess the fit of the model input data distribution to the distributions of measured soil Cd concentration, soil pH, TC content and bulk density. These were assumed to be log-normal, normal or Weibull (Table D5 and Figure D1 in Appendix). The non-soil variables included precipitation excess, P fertiliser application rate and plant yield. The precipitation excess and plant yield were assumed to have a relative standard deviation of 20%. The non-soil variables were assumed to change randomly every year. The Monte-Carlo simulation was run over 10,000 iterations using the R package *tidyverse* (Wickham, 2017).

The modelled soil depths were 7.5 cm for pastoral systems and 15 cm for cropping sites. It was assumed that the contribution of inorganic C to soil total C is insignificant, which is appropriate for NZ soils (Sparling et al., 2008). The model simulated the change of soil Cd concentration over the next 25 years. While the TFMS attempts to reduce increments of Cd accumulation rate in soil over 100 years (to the point (1.8 mg Cd kg^{-1} soil) where no further soil cadmium accumulation is permitted), the model simulations were limited to 25 years for two reasons: (1) given ongoing changes in global climates, attempts to carry out long-term forecasts for Cd accumulation (that are partly informed by climatic conditions) are fraught with an unacceptable level of uncertainty and (2) the model does not consider the possibility of switching to lower Cd concentration fertiliser once certain soil Cd trigger values are reached because this is a decision that would be made according to individual farmer's requirements, therefore, there is a progressively decreasing level of confidence associated with predicting Cd accumulation in soil beyond the concentration of 1 mg kg^{-1} (the Cd trigger value). In this study, a soil Cd concentration of 1 mg kg^{-1} was set as a benchmark to estimate the percentage of farms exceeding this limit where the choice and rate of P fertiliser becomes more restricted. The probability of Cd accumulation was assessed at the 50^{th} and 95^{th} percentile levels. The former indicates the most likely accumulation rate, given the variability in input variables, while the latter accumulation rate allows for a greater margin of safety. Jager et al. (2000) showed that results from higher than the 95^{th} percentile of the probability distributions had the worst deterministic risk quotients when running probabilistic risk assessments. Öberg and Bergbäck (2005) also confirmed that the margin of safe level in uncertainty was significantly reduced when the upper 95^{th} percentile of values were taken into consideration.

5.5 Modelling scenario

5.5.1 Scenario 1: Effect of phosphorus fertilizer cadmium content and soil type on soil cadmium accumulation in dry-stock farming soils

Cd accumulation was simulated in drystock systems (sheep and beef farming) as this land use type occupies a large proportion (31.9 %) of NZ agricultural land (Statistics New Zealand, 2017) and features predominantly on Organic, Pumice, Sedimentary and Volcanic soils. The soils not belonging to the four main soil orders were considered as *Others*. It was assumed that the pasture in these systems consisted of ryegrass, as it comprises ~70% of pasture species (Gray & McLaren, 2005). In NZ, the voluntary limit on the level of Cd in P fertiliser was set at 280 mg Cd kg^{-1} P. Over the period from 2003 to 2015, the data from the NZ fertiliser industry showed that the average Cd concentration in P fertiliser was 184 mg Cd kg^{-1} P. From 2014 to 2015, the monthly mean Cd concentration fluctuated at around 100 mg Cd kg^{-1} P (Taylor et al., 2017). The P maintenance nutrient requirement in drystock systems varies largely between regions, soil types and stocking rates. Butler and Johnston (1997) reported that the average annual P usage rate in Waikato and Bay of Plenty was at 24 kg ha^{-1}, while the rate ranged from 17 - 34 kg ha^{-1} in Canterbury (McDowell, 2012). In this study, three different concentrations of Cd in P fertiliser (100, 184 and 280 mg Cd kg^{-1} P) were applied in the model, with a fixed annual P maintenance application rate at 25 kg ha^{-1}. The model input variables and their probability distributions are shown in Table SD (Appendix).

5.5.2 Scenario 2: Effect of land use and irrigation

Two general types of agricultural land use: pasture (dairy and drystock) and cropping (onion, potato and wheat), were considered under different rates of irrigation and with P fertiliser application rates set at commonly used values for subcategories of these land use types. The Cd concentration in the fertiliser was set as 184 mg Cd kg^{-1} P to reflect the current Cd concentration in P fertiliser. Pasture in the dairy and drystock systems was assumed to be composed of ryegrass (*Lolium perenne*), white clover (*Trifolium subterraneum* L.), plantain (*Plantago lanceolata*) and chicory *Cichorium intybus*) at the ratio of 7 : 2 : 0.5 : 0.5. In cropping systems, the crops were assumed to consist of potato, wheat and onion, which are main dietary plants with relatively larger harvested areas (Statistics New Zealand, 2017). All cropping systems were assumed to be non-rotation. The coefficients of TF in pastoral and cropping plants were estimated from field trial experiments conducted by Cavanagh et al. (2016). As summarised by (Moog, 2009), spray irrigation represented 74% of irrigated pastures. In this model, all additional water from irrigation was assumed to cause Cd downward movement

without water loss via surface runoff or evaporation. The SCM input variables and their probability distributions are given in Table D7 (Appendix).

5.5.3 Scenario 3: Projected regional trends in soil Cd concentrations: Waikato and Canterbury

Both Waikato and Canterbury regions are traditional agricultural areas in NZ, with 28.0% of the total number of NZ dairy cattle in the Waikato, and 19.2% in Canterbury in 2016 (Statistics New Zealand, 2017). Apart from dairy farming, Canterbury is also the main crop growing area. Intensive fertiliser application in these two regions has contributed to high levels of Cd accumulation in some soils. In particular, the agricultural areas of the Waikato region are dominated by Volcanic soils which are well known for their high metal oxide contents with a strong ability to stabilize soil organic C and bind Cd. Hence, the SCM simulated Cd accumulation in these two regions. The modelling parameters used to describe the two regions were obtained from data published by regional councils (Table D8 and Table D9 in Appendix). Given that current median soil Cd concentrations in the Waikato region are over 0.6 mg kg^{-1}, the average annual P application for pasture was assumed to vary between 25 and 45 kg P ha^{-1}, which is close to the amount of maintenance P requirements in dairy systems (2.5 - 3 cows ha^{-1} = approx. 27 - 45 kg P ha^{-1}) according to the P usage guidelines (Roberts & Morton, 2016).

5.6 Results and discussion

5.6.1 Validation of the SCM

The estimated soil Cd concentrations from the SCM model between 1952 and 2003 predicted topsoil Cd concentrations well and coincided closely with the estimations from McDowell (2012) and Salmanzadeh et al. (2017a) (Figure 5.1). However, for the period between 2003 and 2015, predictions from the SCM model were better than the CadBal model used in McDowell (2012) and Salmanzadeh et al. (2017a), as the SCM model predicted a slight increase in soil Cd concentration for this period, which was in agreement with the increased soil Cd concentration in the dryland treatment measured in the Winchmore irrigation trial (Figure 2.5b in Chapter 2), while McDowell (2012) predicted a decline in Cd concentration and Salmanzadeh et al. (2017a) predicted a plateau trend for the same period. The difference between the models (especially after the year of 2003) mainly resulted from the different ways in calculating Cd loss. In terms of the best scenario with the closest correspondence to the measured Cd in Salmanzadeh et al. (2017a), the occurrence of the plateau resulted from the higher estimation of Cd leaching (3.2 rather than 1.6 g ha^{-1} yr^{-1}) applied in CadBal. In the SCM model, the average annual Cd loss via leaching was 3.87 g ha^{-1}, higher than the

values in the studies of both McDowell (2012) and Salmanzadeh et al. (2017a) between 2003 to 2015. In CadBal, the average predicted amounts of soil Cd uptake by herbage and subsequent removal by animal grazing were 1.75 and 1.94 g from 2003 to 2015. This may be overestimated, because the majority of daily Cd intake by sheep is believed to be returned to the soil through faeces (Lee et al., 1996; Sheppard et al., 2009). The SCM modelling results suggested that less than 0.01 g Cd was estimated to have been lost via accumulation in animal biomass every year during this period. When modelling the fertiliser trials, with the integration of annual precipitation excess from 1952 and the utilization of SCM to estimate yearly leaching loss, the SCM predicted soil Cd coincided closely with the measured concentrations reported in previous studies (Kelliher et al., 2017; McDowell, 2012; Salmanzadeh et al., 2017a) (Figure 5.2). Since 2000, the conversion to P fertiliser with lower Cd concentrations made Cd outputs reach a balance with soil inputs, which contributed to the occurrence of the plateau of soil Cd accumulation. During the period of 2003 to 2015, the average estimated annual Cd removal via leaching was 4.24 and 7.19 g in the 17 and 34 kg P ha^{-1} treatments respectively, much larger than the annual loss via animal grazing (*ca.* 0.01 g). These predicted Cd loads in leaching were also much higher than those in outwash, of which McDowell (2010) estimated annual Cd loss via surface runoff was 0.426 and 0.826 g in these two fertiliser treatments respectively.

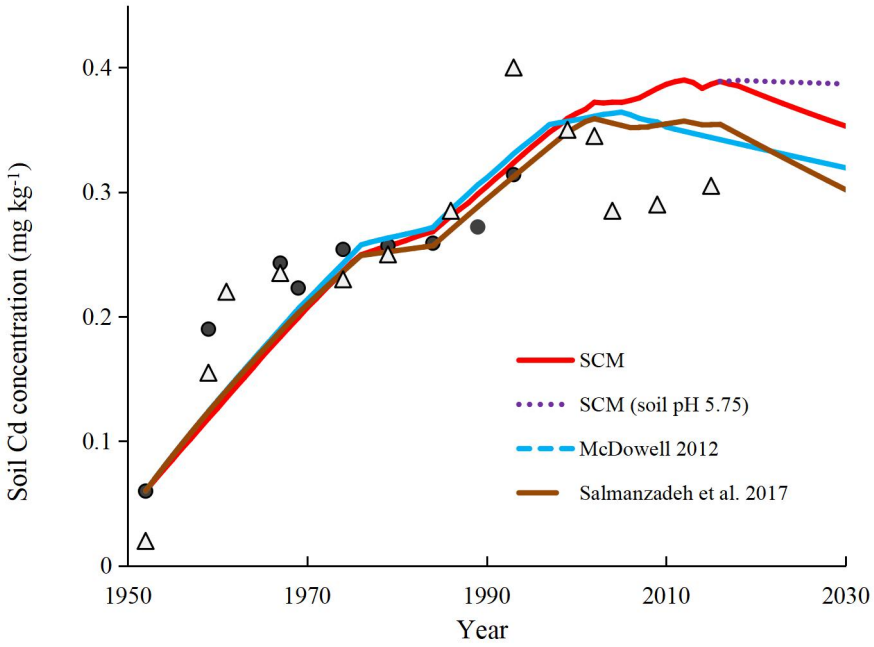

Figure 5.1 Comparison of SCM and CadBal for the Cd changes of topsoils (7.5 cm) in the dryland treatment of the Winchmore irrigation trial from 1952 including a prediction up to 2030 (lines). The average soil Cd concentrations in dryland plots which were measured by McDowell (2012) (●) and Salmanzadeh et al. (2017a) (Δ). Cd data between 1999 and 2006 from McDowell (2012) were excluded due to possible analytical error.

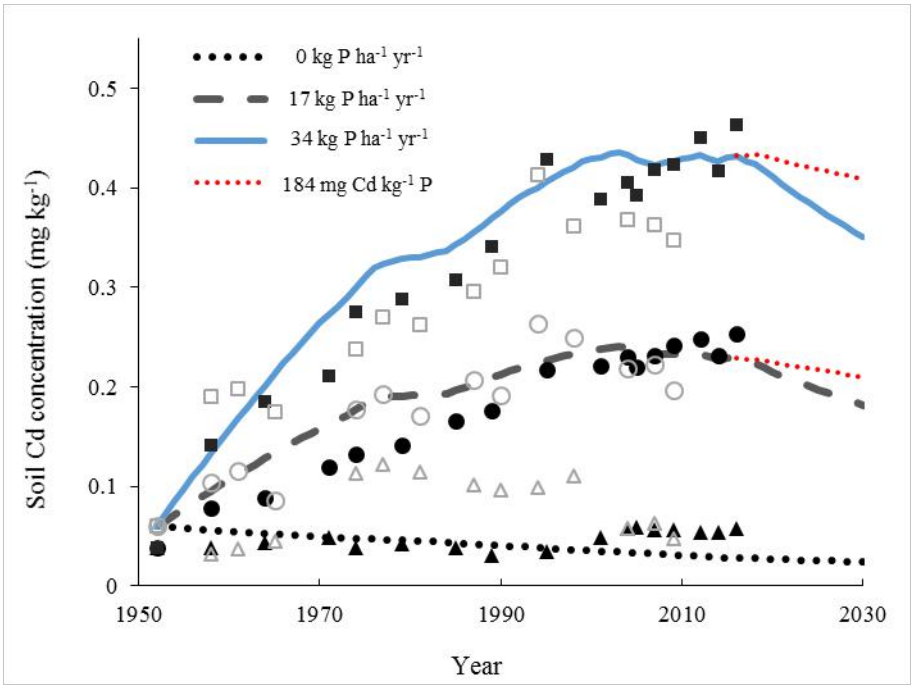

Figure 5.2 Results of the SCM model for the Cd changes of topsoils (7.5 cm) at Winchmore from 1952 including a prediction up to 2030 (lines). The average soil Cd concentrations in Winchmore measured in plots which received no fertiliser (△ from McDowell (2012) and ▲from Gray et al. (2017a) and Kelliher et al. (2017)) or P applications of 17 (○ and ●) and 34 kg P ha^{-1} yr^{-1} (□ and ■). Cd data between 1999 and 2006 from McDowell (2012) were excluded due to possible analytical error.

Similar to CadBal, the SCM simulation also predicted a decline if the P fertiliser with a lower Cd concentration (86 mg Cd kg^{-1} P) was applied from the year of 2015. However, the declining trend of soil Cd concentration resulted from the current comparatively low soil pH (5.20) in the irrigation trial (McDowell, 2010). Sensitivity analysis has shown that soil pH had a considerable effect on the soil Cd mass balance (Six & Smolders, 2014). It is assumed that liming, a general farming practice in NZ, was carried out to maintain soil pH at 5.5 to 6.0 in the Winchmore irrigation trial from 2015. The model results suggested that if the soil pH increased to 5.75, the concentrations of soil Cd would stay constant, rather than decrease (Figure 5.1). In the Winchmore fertiliser trial, the results of the mass balance model also indicated an observed plateau of soil Cd. In the SCM, the slowdown of soil Cd accumulation occurred in 2001 when the fertiliser Cd concentration had decreased to 152 mg Cd kg^{-1} P, 45.9% lower than that in 2000 (281 mg Cd kg^{-1} P) and 55.9% lower than that in the 1960s (345 mg Cd kg^{-1} P). The plateau of soil Cd concentrations supports the conclusion by Kelliher et al. (2017) indicating that Cd accumulation in NZ soils was determined by the fertiliser's Cd concentration and its application rate. Due to a constant level of P application at the Winchmore trials, the reduction in

soil Cd accumulation rate mainly resulted from the maintenance of Cd concentrations in phosphate fertiliser since the mid-1990s (Taylor et al., 2017). However, it is difficult to conclude that there will be no more Cd accumulation, even though a good agreement has been made between predicted and observed Cd concentration. The estimates of potential changes in soil Cd accumulation are often confounded by the large variety of factors. The model suggests that if Cd concentration in P fertiliser was maintained at 184 mg kg^{-1} in the next decade, no significant increase or decrease of soil Cd concentrations would be observed under the two levels of P application in the Winchmore trial soils (Figure 5.2). Meanwhile, alternations of environmental variables increase the uncertainties in long-term predictions. For instance, climate change, that an increasing and more frequent intense winter rainfall has been predicted in the South Island (Ministry for the Environment, 2018), may enhance more Cd loss via leaching and surface runoff in the Winchmore trials in the future. Soil pH and OC concentrations are important parameters determining the modelling Cd output via leaching in the SCM, but their actual values in the future are not easy to predict. In 1972, 4 t ha^{-1} lime addition raised average soil pH from 5.9 to 6.5 in the fertiliser trial (Fraser et al., 2011), while the average soil pH level has dropped to 5.6 in 2016 (Wakelin et al., 2017). Soil acidification occurring naturally in the Winchmore trial can increase soil Cd solubility and enhance Cd loss via leaching. It is not clear whether liming will be used again to ameliorate soil acidity in the future. Soil total C contents have increased from 2.66% in 1952 to 4.31% in 2016, and are likely to continue to increase (Schipper et al., 2013; Wakelin et al., 2017). Soil bulk density has been indicated to decrease from 1.16 g cm^{-3} in 1968 to 0.91 g cm^{-3} in 2016 (Gray et al., 1999b; Kelliher et al., 2017). The surfaces of soil OC are generally negatively charged, due to the presence of functional groups, including COOH-, -OH and -SH, which can bind Cd (Loganathan et al., 2012). Gray et al. (1999b) showed that more than 40% of Cd in the Winchmore fertiliser trial was associated with soil organic matter fractions. Hence, an increasing soil OC content and declining soil bulk density will enhance the Cd sorption capacity of soil particles .

5.6.2 Effect of phosphorus fertiliser cadmium content and soil order on soil cadmium accumulation in drystock farming soils

The SCM simulations indicate that if fertiliser Cd concentrations are maintained at the current level 184 mg kg^{-1} P, the greatest proportional increase in median Cd concentration in the future is likely to occur in Organic soils with a 20.25% of increase. In 25 years, 42.55% of soil Cd concentrations are estimated to exceed 1 mg kg^{-1} (Table 5.2). Under the same conditions, sedimentary soils and soils not belonging to the four main soil orders considered (i.e. *Others*) experience the smallest changes in the distribution of soil Cd concentrations, here the soils in the top 5^{th} percentile of soil Cd concentrations are not likely to increase due to the increased Cd losses through leaching and plant

uptake; however, the median concentration may continue to increase as the proportional losses in the less contaminated soils remain relatively small. This is supported by the observed plateau in soil Cd accumulation observed at the Winchmore research station. The change in the distribution of soil Cd concentrations of Volcanic and Pumice soils is likely to be negligible, owing to their relatively high initial concentrations (and, hence, high expected rates of Cd loss through crop offtake and leaching); here there is little scope for further accumulation, except in the least contaminated soils. This may explain the observed plateau in soil Cd accumulation on the Volcanic soils of the Waikato region (Taylor et al., 2017). In the case of simulations with a median Cd accumulation rate (50th percentile), the SCM simulations suggest that Volcanic soils subject to the lowest Cd inputs could experience up to a 2.5% decrease in median Cd concentrations and at the 95% percentile for soil Cd concentrations to be lower than 1.30 mg kg^{-1} after 25 years. However, soil Cd is predicted to continue to increase and 43.14% of soil Cd concentration will be higher than 1 mg kg^{-1} if fertiliser's Cd concentration is 280 mg kg^{-1} P within that time. The modelled soil Cd concentrations varied largely between different levels of fertiliser's Cd concentration, confirming the findings (Taylor et al., 2017) that the slowdown of soil Cd concentration in NZ soils mainly resulted from the introduction of voluntary limits for Cd in P fertiliser. This also agrees with Kelliher et al. (2017) who highlighted the importance of Cd concentrations in fertiliser on soil Cd accumulation.

The biggest impact of changes in fertiliser Cd concentrations are likely to occur in Organic soils where the majority of soils have the potential to accumulate Cd, due to their lower soil bulk density and higher Cd binding capacity compared to the other four soil orders. The SCM estimates that an annual 25 kg ha^{-1} P application with a Cd concentration of 184 mg kg^{-1} P can increase the soil Cd concentration at yearly rate of 10.18 μg kg^{-1} if no Cd loss is taken into consideration. This is higher than in Pumice (8.79 μg kg^{-1}), Volcanic (7.20 μg kg^{-1}), Sedimentary (5.47 μg kg^{-1}) or Other soils (6.06 μg kg^{-1}) (Table S10 in Appendix). Meanwhile, the modelled 50th percentile rate of Cd loss via leaching in Organic soils is 2.90 μg kg^{-1}, over 40% lower than that in Volcanic and Pumice soils when the Cd concentration in P fertiliser is 184 mg kg^{-1} P. Different from Volcanic soils with relatively high Fe and Al mineral contents to bind phosphate, low concentrations of mineral matter in organic soils contribute to its low anion storage capacity, but its high organic C concentrations are well known in binding Cd (Al Mamun et al., 2016). Compared to other soil orders, lower Cd leaching rates of Organic soils were also observed in Cd leaching studies. Gray and McDowell (2016) found that the annual Cd load leached from organic soils (total Cd concentration, 0.08 mg kg^{-1}) fluctuated between 0.14 and 0.21 g ha^{-1}, which was lower than that in Pumice (0.35 g ha^{-1}), Allophanic (0.86 g ha^{-1}), Brown (0.54 g ha^{-1}), Pallic (0.27 g ha^{-1}), and Recent (0.5 - 0.8 g ha^{-1}) soils (Carrick et al., 2014; Gray et

al., 2003b). In New Zealand, organic soils cover about 258,748 ha, covering around 1% of total NZ area. They are particularly important in the Waikato region where they comprise 4.0% of total area (Dresser et al., 2012). The increase of the percentage of soil with Cd concentration exceeding 1 mg kg^{-1} implies that the greatest relative benefit of using fertilisers with low Cd concentrations is likely to be achieved on Organic soils.

5.6.3 Effect of land use and irrigation

The SCM results indicate that under no irrigation the percentage of soils with Cd concentrations exceeding 1 mg kg^{-1} in the dairy system at the 50^{th} percentile level of accumulation rate after 25 years is 22.6%, which is over seven times higher than the other agricultural systems under the same conditions (Table 5.3). In 25 years' time, dairy soils have the largest proportional increase in the 50^{th} percentile Cd concentration with 21.2% of growth if no irrigation is applied. Under a similar pasture farming system with the same modelling soil depth, the median Cd concentration in drystock soils is estimated to show a continuous increase, but the soils in the top 5^{th} percentile of soil Cd concentrations may experience a slight decline due to greater leaching losses. Compared to pasture soils, soil Cd concentrations in cropping systems experience smaller changes in the distribution of soil Cd concentrations, due to a deeper soil depth which may dilute additional Cd. The change of Cd concentrations in potato soils is likely to be smaller than that in onion soils, although a larger amount of P usage is applied for potato farming. The relatively higher yield and larger value of Cd soil/plant transfer factor of potato may contribute to higher rates of Cd loss through crop offtake (Table 5.1b).

The SCM results suggest that there is potential for Cd accumulation in the soils under all cropping farming systems at the 50^{th} percentile accumulation rate, with an inverse relationship between irrigation rate and Cd accumulation (Table 5.3). Conversely, the Cd concentrations in the 5% of the most contaminated soils used for pasture are likely to decrease over the next 25 years, due to the relatively high combined losses of Cd from leaching. This partly agrees with previous findings which suggested that leaching of Cd may be a significant loss pathways for the contaminant from irrigated pasture soil (Salmanzadeh et al., 2017a; Salmanzadeh et al., 2017b), although it is important to note that the median concentrations may still increase under all but the highest irrigation rates.

Table 5.2 SCM-predicted changes in soil Cd concentrations in different soil orders when subject to variable amounts of Cd in P fertiliser over the next 25 years. The results are shown as percent change from the corresponding percentile level of the initially modelled soil Cd distribution when subject to accumulation rates at two levels of risk (50th and 95th percentile). The current and predicted percentages of soils exceeding the 1 mg kg^{-1} Cd concentration threshold at the two accumulation rates are also shown.

Soil order	Cd concentration in fertilizer (mg Cd kg^{-1} P)	Distribution of measured results [@]			Model-predicted distributions of concentrations at two accumulation rates after 25 years					
					50th percentile accumulation rate			95th percentile accumulation rate		
		50th percentile Cd conc. (mg kg^{-1})	95th percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50th percentile Cd conc. (mg kg^{-1})	95th percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50th percentile Cd conc. (mg kg^{-1})	95th percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}
Organic	100	0.79	1.34	27.66%	0.85	1.38	31.91%	0.93	1.52	38.30%
	184				0.95	1.53	42.55%	1.10	1.79	60.64%
	280				1.07	1.72	57.45%	1.35	2.18	76.60%
Pumice	100	0.53	1.04	5.94%	0.52	0.91	2.97%	0.57	1.05	6.44%
	184				0.57	0.99	4.46%	0.63	1.16	7.92%
	280				0.63	1.09	7.92%	0.71	1.29	16.34%
Sedimentary	100	0.21	0.79	2.14%	0.22	0.74	1.39%	0.23	0.82	2.31%
	184				0.23	0.78	1.74%	0.25	0.87	3.18%
	280				0.25	0.83	2.26%	0.27	0.94	3.99%
Volcanic	100	0.81	1.46	31.67%	0.79	1.30	25.33%	0.87	1.53	37.86%
	184				0.86	1.41	34.56%	0.96	1.67	46.17%
	280				0.93	1.53	43.14%	1.09	1.86	57.12%
Others	100	0.29	0.96	4.42%	0.30	0.86	1.68%	0.31	0.99	4.78%
	184				0.31	0.91	3.01%	0.34	1.06	6.11%
	280				0.34	0.98	4.69%	0.37	1.16	8.23%

[@] Data from the Fertilizer Association of New Zealand (Cavanagh, 2014).

Table 5.3 SCM-predicted changes in soil Cd concentrations in soils under different land uses and irrigation rates over the next 25 years. The results are shown as percent change from the corresponding percentile level of the initially modelled soil Cd distribution.

Landuse (median P application rate, kg P ha^{-1} yr^{-1})	Irrigation (m)	Distribution of measured results [@]			Model-predicted distributions of concentrations at two accumulation rates after 25 years					
					50^{th} percentile accumulation rate			95^{th} percentile accumulation rate		
		50^{th} percentile Cd conc. (mg kg^{-1})	95^{th} percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50^{th} percentile Cd conc. (mg kg^{-1})	95^{th} percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50^{th} percentile Cd conc. (mg kg^{-1})	95^{th} percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}
Dairy -45	0	0.52	1.27	16.08%	0.63	1.38	22.60%	0.71	1.59	31.34%
	0.30				0.57	1.13	12.44%	0.66	1.41	25.26%
	0.60				0.53	0.96	2.82%	0.62	1.29	20.48%
Dry-stock -25	0	0.24	0.89	3.60%	0.27	0.88	3.04%	0.29	0.98	4.88%
	0.15				0.26	0.80	0.88%	0.28	0.95	4.56%
	0.30				0.25	0.74	0.32%	0.27	0.92	3.68%
Onion -60	0	0.21	0.72	1.78%	0.24	0.79	2.17%	0.25	0.85	3.16%
	0.15				0.23	0.77	1.98%	0.25	0.83	2.37%
	0.30				0.23	0.75	1.78%	0.25	0.82	2.17%
Potato -75	0	0.21	0.72	1.78%	0.23	0.74	0.79%	0.25	0.79	1.98%
	0.15				0.23	0.72	0.79%	0.25	0.78	1.78%
	0.30				0.23	0.70	0.59%	0.24	0.77	1.78%
Wheat -50	0	0.21	0.72	1.78%	0.23	0.75	1.78%	0.24	0.79	2.17%
	0.15				0.22	0.73	0.79%	0.24	0.78	1.98%
	0.30				0.22	0.71	0.79%	0.23	0.77	1.78%

[@] Data from the Fertilizer Association of New Zealand (Cavanagh, 2014).

5.6.4 Trends in soil Cd concentrations in the Waikato and Canterbury regions

Under the most likely condition (50th percentile accumulation rate), the model results suggest that P fertiliser application at rates of 35 and 45 kg P ha^{-1} will increase soil total Cd concentrations of dairy soils in the Waikato region, with a yearly mean accumulation rate of 4.4 and 7.2 μg Cd kg^{-1} soil year^{-1} over the next 25 years. However, a plateau in soil Cd concentrations may be encountered at the lower application rate of 25 kg P ha^{-1} (Table 5.4). These soil Cd accumulation rates are much smaller than the annual rate of 22 μg Cd kg^{-1} soil estimated by Kim (2005). Similar results are estimated in cropping soils where Cd concentrations are predicted to increase at 3.6 and 5.6 μg Cd kg^{-1} year^{-1} soil in potato systems if 70 and 90 kg P ha^{-1} are applied yearly, which are much lower than 9.0 μg Cd kg^{-1} soil reported in Kim (2005). Smaller Cd accumulation rates in the SCM simulations coincide well with the reductions of P usage and fertiliser Cd concentration in Waikato. In the 1990s, annual P usage of each hectare in Waikato and Bay of Plenty was estimated at 56 kg for dairy, 24 kg for drystock and 147 kg for vegetable farms (Butler & Johnston, 1997). However, continuous Cd accumulation may still raise soil total concentrations in the next 25 years. Annual 45 kg P ha^{-1} application can increase median Cd concentrations of dairy soils to 1.01 mg kg^{-1} (95th percentile, 1.62 mg kg^{-1}), with 50.21% of soils exceeding 1 mg kg^{-1} after 25 years. The predicted on-going Cd accumulation in the Waikato confirms the observed results in Waikato dairy farms, where average soil Cd concentrations in the older dairy blocks were significantly greater than the newer blocks (Stafford et al., 2018c). However, discrepancies were indicated between the modelling results and measured results from Taylor et al. (2017), because no evidence has shown that the P annual usage in dairy farm decreases to 25 kg P ha^{-1}. The discrepancies may firstly due to soil erosion. Owing to the intensive rainfall and hilly landscape, the estimated mean amount of soil erosion in Waikato is considerable (4,640 kg ha^{-1}) in grassland, much higher than in Canterbury and Southland (Dymond et al., 2010). For example, erosion was estimated to cause only 50 kg ha^{-1} soil loss from the top 7.5 cm horizon in a sheep farm in Canterbury (McDowell & Wilcock, 2008). Secondly, monitoring sites in the Waikato also cover unfertilised and less P fertilised soils, such as forest soils.

Increasing at the 50th percentile accumulation rate, the Cd concentrations in Canterbury were predicted not to exceed 1 mg kg^{-1} for five kinds of land use if irrigation is applied in the next 25 years, although the median soil Cd concentration is likely to experience a slight increase, except at the rate of 25 kg ha^{-1} P application in dairy system (Table 5.5). Corresponding to the same P usage levels, the SCM simulations indicate that non-irrigation enhances more soil Cd accumulation, however, its effect on the percentage of soils with Cd concentration higher than 1 mg kg^{-1} may be negligible. In the case of the largest P usage (55 kg ha^{-1}·year^{-1}) in dairy farms with the 50th percentile Cd

accumulation rate, 95% percentile for soil Cd concentrations are estimated lower than 0.78 mg kg^{-1} after 25 years. The risk of the Cd concentration exceeding the assumed maximum guideline value (1.0 mg kg^{-1}) is comparatively low. This is mainly because Canterbury is dominated by sedimentary soils with lower soil pH and OC contents, which contributes to a higher Cd loss via leaching and crops offtake and consequently lower its Cd accumulation rate (see discussion in Section 3.5). Also, due to the development of intensive farming but a relatively low rainfall, Canterbury has the largest area of irrigated land (507,420 hectares) consisting of 63.8% of the total NZ irrigated area. Salmanzadeh et al. (2017b) found that irrigation could induce an 11 g Cd loss annually (including leaching or outwash) from the top 10 cm soil horizon.

Table 5.4 SCM-predicted changes in soil Cd concentrations in soils under different land uses and fertiliser usage in the Waikato region. The results are shown as percent change from the corresponding percentile level of the initially modelled soil Cd distribution.

Landuse	P usage (kg ha^{-1})	Distribution of measured results [@]			Model-predicted distributions of concentrations at two accumulation rates after 25 years					
					50^{th} percentile accumulation rate			95^{th} percentile accumulation rate		
		50^{th} percentile Cd conc. (mg kg^{-1})	95^{th} percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50^{th} percentile Cd conc. (mg kg^{-1})	95^{th} percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50^{th} percentile Cd conc. (mg kg^{-1})	95^{th} percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}
Dairy	25	0.83	1.48	33.48%	0.88	1.42	36.17%	0.99	1.67	47.94%
	35				0.94	1.52	43.26%	1.09	1.83	58.16%
	45				1.01	1.62	50.21%	1.21	2.00	65.96%
Drystock	15	0.57	1.26	19.67%	0.58	1.12	16.39%	0.62	1.30	21.86%
	25				0.62	1.21	19.67%	0.68	1.39	26.23%
	35				0.66	1.29	22.95%	0.74	1.52	31.15%
Potato	50	0.64	0.99	6.52%	0.67	1.00	6.52%	0.72	1.09	10.87%
	70				0.72	1.07	10.87%	0.78	1.19	23.91%
	90				0.76	1.14	21.74%	0.85	1.29	32.61%
Onion	40	0.64	0.99	6.52%	0.69	1.02	6.52%	0.74	1.11	13.04%
	60				0.73	1.08	10.87%	0.80	1.20	26.09%
	80				0.78	1.16	21.74%	0.87	1.31	32.61%

[@] Data from the Fertilizer Association of New Zealand (Cavanagh, 2014).

Table 5.5 SCM-predicted changes in soil Cd concentrations in soils under different land uses and fertiliser usage in the Canterbury region. The results are shown as percent change from the corresponding percentile level of the initially modelled soil Cd distribution.

Landuse	P usage (kg ha^{-1})	Distribution of measured results [@]			Model-predicted distributions of concentrations at two accumulation rates after 25 years					
					50th percentile accumulation rate			95th percentile accumulation rate		
		50th percentile Cd conc. (mg kg^{-1})	95th percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50th percentile Cd conc. (mg kg^{-1})	95th percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}	50th percentile Cd conc. (mg kg^{-1})	95th percentile Cd conc. (mg kg^{-1})	Percentage of soils exceeding 1 mg kg^{-1}
Dairy	25 *i* [a]	0.22	0.69	2.17%	0.21	0.54	0.00%	0.23	0.61	0.00%
	25				0.24	0.68	2.17%	0.24	0.73	2.17%
	40 *i*				0.23	0.56	0.00%	0.24	0.65	1.09%
	40				0.25	0.73	2.17%	0.26	0.79	2.17%
	55 *i*				0.24	0.59	0.00%	0.26	0.69	2.17%
	55				0.27	0.78	2.17%	0.28	0.85	3.26%
Drystock	15 *i*	0.15	0.27	0	0.15	0.26	0.00%	0.16	0.28	0.00%
	15				0.16	0.28	0.00%	0.16	0.29	0.00%
	25 *i*				0.16	0.27	0.00%	0.16	0.29	0.00%
	25				0.16	0.29	0.00%	0.17	0.30	0.00%
	35 *i*				0.16	0.28	0.00%	0.17	0.30	0.00%
	35				0.17	0.31	0.00%	0.18	0.32	0.00%
Onion	80	0.19	0.44	0	0.20	0.43	0.00%	0.20	0.45	0.00%
	60				0.21	0.45	0.00%	0.21	0.48	0.00%
	40				0.22	0.47	0.00%	0.22	0.50	0.00%
Potato	50	0.19	0.44	0	0.19	0.40	0.00%	0.20	0.43	0.00%
	70				0.20	0.42	0.00%	0.21	0.45	0.00%
	90				0.21	0.44	0.00%	0.22	0.47	0.00%
Wheat	30	0.19	0.44	0	0.19	0.42	0.00%	0.20	0.44	0.00%
	50				0.20	0.44	0.00%	0.21	0.46	0.00%
	70				0.22	0.49	0.00%	0.22	0.49	0.00%

i stands for irrigation and its rates are shown in Table S9 in Appendix. [@] Data from the Fertilizer Association of New Zealand (Cavanagh, 2014)

5.6.5 The implication of the SCM model on environmental significance

The SCM model highlights the importance of Cd concentration in P fertiliser and P fertiliser application rate on soil Cd accumulation, which agrees with previous work that has employed the same mass balance model to predict soil Cd concentration (Sterckeman et al., 2018). If current farming practices continue in the next 25 years, the results from the SCM model indicate that soils in the Winchmore fertiliser trial will meet a plateau of soil Cd concentrations, which is different from a predicted decline of soil Cd concentration in European soils (Six & Smolders, 2014), but agrees with an increasing Cd concentration in French cropping systems (Sterckeman et al., 2018), this estimated increase of soil Cd concentration in NZ cropping soils may be also due to a higher P application rate and a higher Cd concentration in P fertiliser in NZ than in Europe. Under the median level of P usage, the predicted increase of Cd concentration in both Waikato and Canterbury agricultural soils indicates that the soil contamination by Cd would increase. In the Waikato region, the percentages of soils exceeding 1 mg kg^{-1} in dairy, potato and onion soils are predicted to increase, while this percentage in soils used for drystock farming tends to be stable. In order to maintain agronomic P applications rates for productivity, the estimated increase of soil Cd concentration highlights the necessity of a further reduction of Cd concentration in superphosphate, or using non-sulphuric acid derived P fertiliser products. In Europe, the average of Cd concentration in P fertiliser is < 95 mg kg^{-1} (Six & Smolders, 2014). There is some scope to reduce the current Cd concentration in P fertiliser (184 mg Cd kg^{-1} P) used in NZ. Mortvedt (1996) reported that a negligible amount of Cd was lost with the by-products in the production process of P fertilisers. This shows that the Cd concentration in P fertiliser is determined by the Cd/P ratio in rock phosphate (Nziguheba & Smolders, 2008). The use of lower Cd-containing phosphate rock in producing less Cd fertiliser will increase the cost of fertiliser production. Further research is required to consider whether using expensive low Cd fertiliser in NZ will make agricultural products more expensive and harder to export.

In Canterbury, sedimentary soils with relatively low soil pH and organic C concentration contribute to less Cd sorption by soil particles. This implies that more additional fertiliser Cd is removed out from soils by plant uptake and leaching. The results reported by Cavanagh et al. (2016) showing that the Cd concentration in potatoes grown in Canterbury was three times higher than that in Pukekohe (close to Waikato) and one time higher than that in Waikato ($P < 0.05$), support this rationale. Similar higher soil-to-plant transfer factors ($T_{fs} > 1$) in sedimentary soil were also found in ryegrass (Gray et al., 1999a), plantain and chicory (Cavanagh et al., 2016). Therefore, despite generally low soil Cd concentration, further consideration of Cd risk in Canterbury soil should be more focused on Cd concentration in plants, drinkable water and sediment.

5.6.6 Uncertainties of the model in long-term predictions

The SCM indicates that leaching accounts for most Cd loss from topsoils, consistent with the results in some international Cd mass balance models (de Vries & McLaughlin, 2013; Sheppard et al., 2009; Six & Smolders, 2014). In NZ, however, McDowell (2010) estimated Cd loads in surface outwash from flood irrigated pastures were at least as great as leaching losses. Due to the shortage of information on the volume of water loss via surface runoff and its Cd concentration, the surface runoff Cd losses were not included in the SCM. Besides, soil erosion and soil ingestion by animals which also affect soil Cd mass balance were also not considered in the SCM.

The uncertainties of the SCM model are also due to the simplified assumptions of the input parameters, including both Cd inputs and Cd outputs. These model components are site- and farming management- specific, which implies that using default values of each model parameters may increase the uncertainties. These specific farm management practise can change soil properties, and subsequently affect soil Cd concentrations. For example, crops cultivation and drainage normally contribute to a marked decrease in soil OC concentrations (Sparling et al., 1992). In the dairy system, Schipper et al. (2010) observed a significant positive correlation between soil OC loss and stocking rates, fertiliser inputs and removal of C in exported products. Additionally, the application of lime to the topsoil is well practised to neutralise soil acidity in low pH soils (Valentinuzzi et al., 2015).

Concentrations of extracted Cd have been linked to soil pH, OC and total Cd concentration in NZ soils (Gray & Mclaren, 2006; Gray et al., 1999d), however, there is insufficient data available to calibrate the coefficients of partitioning of Cd between the solid phase and solution phase (K_d) against various soil types, specifically those found in NZ. Although this model has been validated with measured soil Cd concentrations in the Winchmore trials, further work is needed to establish the extent to which the empirical equation (Eq. 10) evaluating partitioning of Cd between soil and water to soil pH and organic C concentration of topsoil can accurately represent other NZ soils.

5.7 Conclusion

The SCM has been shown to predict soil Cd accumulation in Winchmore fertiliser and irrigation (dryland treatment) trials. Similar to CadBal, the SCM confirms that a balance is occurring between Cd inputs and Cd loss in the Winchmore pastoral trial. However, the SCM suggests that leaching is the most important process governing Cd output, while the effect of Cd removal via plants on Cd accumulation is negligible, especially in pasture systems.

The SCM simulations suggest that fertiliser Cd concentration plays an important role in soil Cd enrichment. The accumulation rate of soil Cd is influenced by soil order. Due to high soil C content and low bulk density, changes in soil Cd concentration induced by additional fertiliser Cd are the largest in organic soils, while the lowest in sedimentary soils. Irrigation inducing Cd leaching poses negative effects on the increase of soil Cd concentration. Using the choice and rate of fertiliser products allowed for when following the TFMS, the soil Cd concentration in the Waikato will experience a slight increase while no obvious upward tendency of soil Cd is predicted in Canterbury. Although there are both high levels of P application in dairy and cropping systems, a shallower modelling soil depth in the dairy system can amplify the effects of additional fertiliser Cd on soil Cd accumulation. In the next 25 years, if P fertiliser application is at a yearly rate of 45 kg P ha^{-1}, over 50% of dairy farms in the Waikato are likely to reach 1.0 mg Cd kg^{-1} soil therefore will need to switch to a phosphoric acid derived or nitric acid derived fertiliser (with lower assumed Cd concentration) to maintain same rate of phosphorus application, according to the TFMS. In a national level of the dairy system, this percentage is 22.6% if no irrigation is applied.

Chapter 6

Cadmium uptake by onions, lettuce and spinach in New Zealand: Implications for management to meet regulatory limits

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My contribution to this article: I completed most of the laboratory work on soil and plant sample analysis. I collated the data from the field survey samples and joined the discussion for the writing of this manuscript.

6.1 Introduction

Plant uptake of cadmium (Cd) from soil is a key factor affecting food chain transfer. The uptake of Cd by plants is influenced by a number of factors, including crop species and cultivar (e.g. Alexander et al., 2006; Guttieri et al., 2015; Sghayar et al., 2015), and the use of low-Cd-accumulating cultivars provides one means to manage Cd in food crops (e.g. Grant et al., 2008; Zhang et al., 2013). Soil properties, including pH, organic matter, salinity, cation-exchange capacity (CEC), clay content, availability of macronutrients, and micronutrients such as zinc (Zn), also influence Cd uptake in plants (e.g. Chaney, 2012; De Meeus et al., 2002; Golia et al., 2008; Grant & Bailey, 1998; McBride, 2002). Identified relationships between soil properties and plant uptake can be used as the basis for setting soil guideline values intended to ensure that human health is protected when home-grown produce is consumed, and intended to support food standards being met (de Vries & McLaughlin, 2013; de Vries et al., 2007; Römkens et al., 2011; Römkens et al., 2009; Smolders et al., 2007; Swartjes, 2007; Yang et al., 2016). Further, these relationships can indicate the likely efficacy of potential management options for reducing plant uptake of Cd; so far pH management (through lime addition) and the addition of organic matter (as compost) are most common (e.g. Bolan & Duraisamy, 2003; Kumarpandit et al., 2017).

There is concern worldwide regarding the accumulation of Cd in agricultural soils, particularly in relation to the potential adverse effect Cd can have on food quality, leading to dietary or trade risks where food standards are not met (EFSA Panel on Contaminants in the Food Chain, 2011; European

Food Safety, 2012; Lin et al., 2015; Rizwan et al., 2017; Tóth et al., 2016). In New Zealand a strategy for managing the risks of Cd to agriculture and horticulture has been in place since 2011 (MAF, 2011). The strategy aims to "ensure that cadmium in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years". A key component of the strategy is the Tiered Fertiliser Management System (TFMS), which comprises five tiers and four trigger concentrations to minimise Cd accumulation in soil by imposing increasingly stringent fertiliser management practices as Cd concentrations increase.

However, the trigger values are interim given a lack of New Zealand-specific data on soil Cd concentrations that may pose a risk for local agricultural systems and how these risks might be managed (MAF, 2011). Soil Cd concentrations to support compliance with food standards may often be lower than soil Cd concentrations causing detrimental effects on ecological receptors, including plants and soil biota (Cavanagh et al., 2013; de Vries et al., 2007; MPI, 2012). Furthermore, food standards have previously been reported to have been occasionally exceeded in potatoes (Kim, 2005) and wheat grown in New Zealand (Gray et al., 2001) and our other papers discuss soil and plant factors influencing Cd uptake in these crops (Gray et al., 2019a; Gray et al., 2019b).

Onions (*Allium cepa*) are one of the highest-value export crops for New Zealand, valued at $112 million in 2017 (Plant and Food Research., 2017). There are few studies on Cd uptake by onions, possibly because Cd concentrations in onions are relatively low and they represent a small contribution to dietary intake (e.g. European Food Safety, 2012; Pearson et al., 2018). However, regulatory maximum levels (MLs) established for onions are also low(e.g. 0.05 mg kg^{-1} FW, CODEX, 2018; European Commission, 2006), arguably leading to a greater potential for these to be exceeded. For example, in 2016 five shipments of US onions were rejected at the Taiwanese border due to non-compliance with Taiwan's food safety standards for Cd of 0.05 mg kg^{-1} FW.[1]

Leafy green vegetables such as lettuce (*Lactuca sativa*) and spinach (*Spinacia olearacea*), which typically accumulate significantly more Cd in their edible parts than other vegetables (Alexander et al., 2006; Baldantoni et al., 2016; He & Singh, 1994), potentially provide a sensitive indicator for assessing the risk posed by soil Cd in relation to compliance with food standards. Numerous studies have assessed Cd uptake in lettuce, with some also assessing variations between cultivars (Alexander et al., 2006; Li et al., 2014; Zhang et al., 2013). Fewer studies report on the variation in Cd uptake by different lettuce 'types', with lettuce generally grouped into crisphead, buttterhead or buttercrunch, romaine/cos, and loose-leaf types. Crews and Davies (1985) identified that crisphead lettuce, which

[1] https://www.wga.com/blog/exported-us-onions-violate-taiwanese-food-standards-requirements.

comprises the bulk of New Zealand lettuce production, had lower Cd concentrations compared with three other lettuce types. Spinach, as baby-leaf (immature spinach) or bunching (mature) spinach, is a widely consumed leafy green vegetable, globally as well as in New Zealand, and it is frequently identified as one of the highest Cd accumulating vegetables (e.g. Lin et al., 2015).

The objectives of this study were to (i) determine the baseline concentrations of Cd in onions, lettuce and spinach grown in the main commercial growing areas in New Zealand, and (ii) assess the influence of plant and soil factors on Cd uptake in these crops to inform management strategies, including the development of risk-based soil guideline values, to support compliance with regulatory food quality standards.

6.2 Methods

6.2.1 Sites and sampling

Cultivars selected for sampling were those identified by industry grower groups as commonly grown in New Zealand. Onions were all sampled from commercial crops. Cadmium concentrations were determined in four onion cultivars (*Rhinestone* [BV1], *Plutonis* [BV2], *RLK-X1* [BV3], and *Red* [RV1]) grown across three sites in 2015, and in one onion cultivar (*Rhinestone*) grown across 25 additional sites over 2016/17. Leafy greens were sampled from commercial crops, where possible, with seed for specific cultivars provided to other growers and grown as field trials at additional commercial sites. For lettuce, Cd concentrations were determined in three crisphead (Iceberg) cultivars (Constanza [V1], Icegreen [V2] and Vegas [V3]), grown at two sites in 2015, and in three lettuce types (eight lettuce sub-types) (loose-leaf: Red Frill [FR], Green Frill [GF]; romaine/cos: Green Cos [GC], Red Cos [CR), Baby Cos [BC]; crisphead: Iceberg [IB]), grown across five sites in 2016/17. Cadmium concentrations were determined in one spinach cultivar (*Jedi*) sampled across 18 sites in 2016/17, with two additional spinach cultivars (*Black Glove*, *Nightfall*) sampled from one site on separate occasions. Sampling details are summarised in Table 6.1, and general locations are shown in Figure E1 (Appendix).

Table 6.1 Summary of sites and details of soil and plant sampling

Crop	Year/Study type	Sites	Region (no of sites)	No. of cultivars	Sampling details
Onion (*Allium cepa*)	2015– Cultivar study	3 commercial field sites	Pukekohe Waikato Canterbury	2 4 2	For each cultivar present at each site, 4 plots (approx. 600 × 600 mm) were established randomly across the field. Sampling was undertaken just subsequent to lifting. Within each plot, 5 onions and 5 soil cores (25 × 150 mm depth) were collected and combined to form a single composite plant or soil sample, respectively. In addition, a composite soil sample (25 × 150 mm) was taken along a 50 m transect.
	2016 /17– Field survey	25 commercial field sites	Canterbury (8) Hawke's Bay (6) Pukekohe (6) Waikato (5)	1	At each site 3 plots were established randomly across the field and sampled as described above.
Lettuce (*Lactuca sativa*)	2015– Cultivar study, crisphead lettuce	Field trial at 2 commercial field sites	Pukekohe Gisborne	3 3	Four replicate plots containing 6 plants for each cultivar were arranged in a randomised design. Sampling was undertaken at the time of commercial harvest, with 4 lettuces and 5 soil cores (25 × 150 mm depth) collected and combined to form a single composite plant or soil sample. In addition, a composite soil sample (25 × 150 mm) was taken along a 50 m transect.
	2016 /17– Lettuce type study	3 commercial regions, 5 sites	Pukekohe (2) Gisborne (2) Canterbury (1)	5 5 4	Three replicate plots (approx. 1 m × bed width) were established randomly along the rows of each cultivar. Sampling was undertaken just prior to harvest, as described above, but with 5 lettuces and 5 soil cores (25 × 150 mm depth).
Spinach (*Spinacia oleracea)*	2016 /17– Field survey	10 commercial field sites	Gisborne (2) Pukekohe (4) Canterbury (2) Hawke's Bay (2)	1 cultivar sampled as baby leaf[1]	Commercial growers: field trial in commercial field or commercial crop. Three plots (approx. 1 m × bed width) were established randomly over field trial area / along the row. Within each plot, spinach leaves (c. 300 g) and 5 soil cores (25 × 150 mm depth) were collected and combined to form a single composite plant or soil sample. In addition, a composite soil sample (25 × 150 mm) was taken along a 50 m transect.
		11 commercial field sites	Auckland (1) Pukekohe (1) Tasman (3) Manawatū (5) Waikato (1)	1 cultivar sampled as bunching spinach[2]	As described above

[1]Immature spinach – commercially harvested by machines (leaf only) after 3-6 weeks of growth, [2]Mature spinach – commercially harvested as the whole plant after 6-12 weeks of growth; [2] Two additional cultivars were also sampled at one site.

6.2.2 Soil and plant analysis

Soils were oven-dried (35°C) until a constant weight obtained and sieved (<2 mm) before analysis. Soil pH was determined in a 1:2 soil:water solution by potentiometric analysis (Blakemore et al., 1987) Exchangeable potassium (K), calcium (Ca), magnesium (Mg) and sodium (Na) were measured in a 1 M neutral ammonium acetate extract (Blakemore et al., 1987), and analysed by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES; Varian 720 ES- USA). Cation Exchange Capacity (CEC) was calculated by summing concentrations of extractable cations and extractable acidity. Bioavailable phosphorous (P as Olsen P) was determined by bicarbonate extraction (Olsen, 1954). Total carbon (C) and nitrogen (N) were determined by combustion using an Elementar Vario-Max CN elemental analyser. Extractable chloride concentrations were measured in a filtered 1:5 soil:water extract by ion chromatography. (Dionex ICS-2100, Thermo Fisher Scientific Inc.). Total extractable concentrations of Cd, Zn, P, aluminium (Al) and iron (Fe) were determined by microwave digestion (MARSXPRESS, CEM Corp.), using nitric acid and hydrogen peroxide as described by Simmler et al. (2013). The digests were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS; Agilent 7500cx) for Zn, P, Al and Fe. Particle size analysis was measured using the pipette method (Claydon, 1989).

Onion roots, leaves and outer skin were removed, and the remaining bulb weighed, dried at 60°C to a constant weight, and weighed again to enable reporting of data on a fresh weight (FW) basis. Lettuce and spinach leaves were washed and excess water removed, weighed, dried at 60°C to a constant weight, and weighed again to enable reporting of data on a fresh weight (FW) basis. Plant samples were ground and digested by microwave digestion in nitric acid and hydrogen peroxide using the method described by Cindrić et al. (2015) prior to analysis of the digests by ICP-MS. Plant concentration data are expressed as fresh weight concentrations unless otherwise specified.

6.2.3 Quality control/assurance

Soil and plant samples were digested in batches of up to 40. Each batch included at least one digestion (procedural) blank. One out of every 20 samples was analysed in duplicate to confirm repeatability of the analysis. Cadmium concentrations in procedural blanks were used to estimate the method detection limit and duplicate analysis of samples were within 5% of each other. The accuracy of soil and plant analysis was assessed using several internal and external certified reference materials including for soil (NIST Montana 2711; Interlab internal WEPAL soil 921; Interlab internal WEPAL soil 981), and plant (NIST 1573a, tomato leaves; ASPAC internal clover; ASPAC

internal beetroot). Analytical results were within 5% of the certified values. The method detection limits were 0.020 mg kg^{-1} and 0.005 mg kg^{-1} in soil and plant material on a dry weight basis, respectively.

6.2.4 Soil–plant relationships

We assessed the relationship between plant Cd uptake and soil properties using two approaches. Firstly, we tested Freundlich-type regression relationships (Equation 1), with significant soil properties identified through multiple linear regression (see 'Statistical analysis').

$$\text{Log10}(Cd_{plant}) = a + b.pH + c.\text{log10}(Cd_{soil}) + d.\text{log10}(C) + \ldots. \quad (1)$$

Where Cd_{plant} is the plant Cd concentration (mg/kg DW), Cd_{soil} is the soil Cd concentration (mg/kg) and *C* is the soil carbon content (%). We also calculated the plant uptake factors (PUF) (Equation 2) a commonly used, simple measure of plant uptake of inorganic contaminants.

$$\text{PUF} = \frac{\text{Cd}_{\text{plant}}\ (\text{mg/kg (DW)})}{\text{Cd}_{\text{soil}}\ (\text{mg/kg})} \quad (2)$$

Soil Cd concentrations at which specific concentrations occur in a given cultivar can be back-calculated from equation 1 (e.g. de Vries et al. 2007, Romkens et al. 2009, 2011) or by rearrangement of equation 2 yielding equation 3, assuming conditions such as soil properties do not change. Using the ML as the target plant concentration ($Cd_{plant\ limit}$), an estimate can be made of the soil concentration at which the food standard may be reached (nCdFS). The food standard is expressed as fresh weight, which requires conversion to a Cd concentration based on dry weight. The dry weight was 10% of the fresh weight for onions, 9% for spinach, 5% for non-iceberg lettuce, and 3% for iceberg lettuce, based on the mean dry matter content for our samples. These values are not intended as threshold limits, but rather provide an insight into soil properties influencing plant uptake and the Cd concentrations at which management to mitigate the risk of exceeding food standards might be considered.

$$nCdFS\ (mg/kg\ ) = \frac{Cd_{plant\ limit}\ (mg/kg\ (DW))}{PUF} \quad (3)$$

6.2.5 Statistical analysis

Statistical analyses were performed using R version 3.4.3 (R Core Team 2016). Multivariate linear regression analyses were a primary focus for assessing the relationship between edible plant Cd concentrations (expressed as dry weight) and soil variables using the MASS and leaps packages

(Lumley, 2017; Venables & Ripley, 2002). Soil properties varied within sites, so analyses were undertaken using individual plot data (where they were available). Where soil properties were measured only once at a given site (e.g. particle size, extractable chloride concentrations), site average data (i.e. the average of the plots sampled on each site) were used to investigate the relationship of those properties with plant concentration.

Regional and cultivar differences in plant Cd concentrations (fresh weight basis) were assessed using ANOVA, or using *t*-tests where only two data sets were compared. Effects were considered significant if they differed at the probability level of 5%, based on Tukey's honest significance difference test (HSD).

6.3 Results and discussion

6.3.1 Lettuce – cultivar and type

Mean lettuce Cd concentrations [1] in three Iceberg cultivars ranged between 0.005 and 0.019 mg kg^{-1} (*n* = 24) with significantly higher Cd concentrations observed in the Iceberg V1 cultivar compared with that in V2 and V3 cultivars for lettuce grown in Gisborne (Figure E2 in Appendix). Given the low Cd concentrations observed in the Iceberg cultivars, a wider range of lettuce types were subsequently sampled. Mean Cd concentrations in all lettuce types ranged between 0.005 and 0.034 mg kg^{-1}, with an overall mean of 0.02 (*n* = 47) (Figure 6.1). Significant differences in Cd concentrations in different lettuce varieties grown at the same site in Pukekohe and Canterbury were not consistent across the sites (Figure 6.1A, C) and no significant differences in Cd concentrations were observed for lettuce varieties grown at the same site in Gisborne (Figure 6.1B). Cadmium concentrations in Iceberg lettuce grown at different sites in Pukekohe and Gisborne were similarly low or lower than concentrations in other lettuce types from those regions (Figure 6.1). Similarly, Iceberg lettuce grown in Canterbury had lower concentrations than other lettuces at this site. However, the lower concentrations in Iceberg lettuce may be more attributable to differences in dry matter content (typically 3% for Iceberg lettuce and 5% for other lettuce types), as no significant difference was observed in Cd concentrations expressed on a dry weight basis.

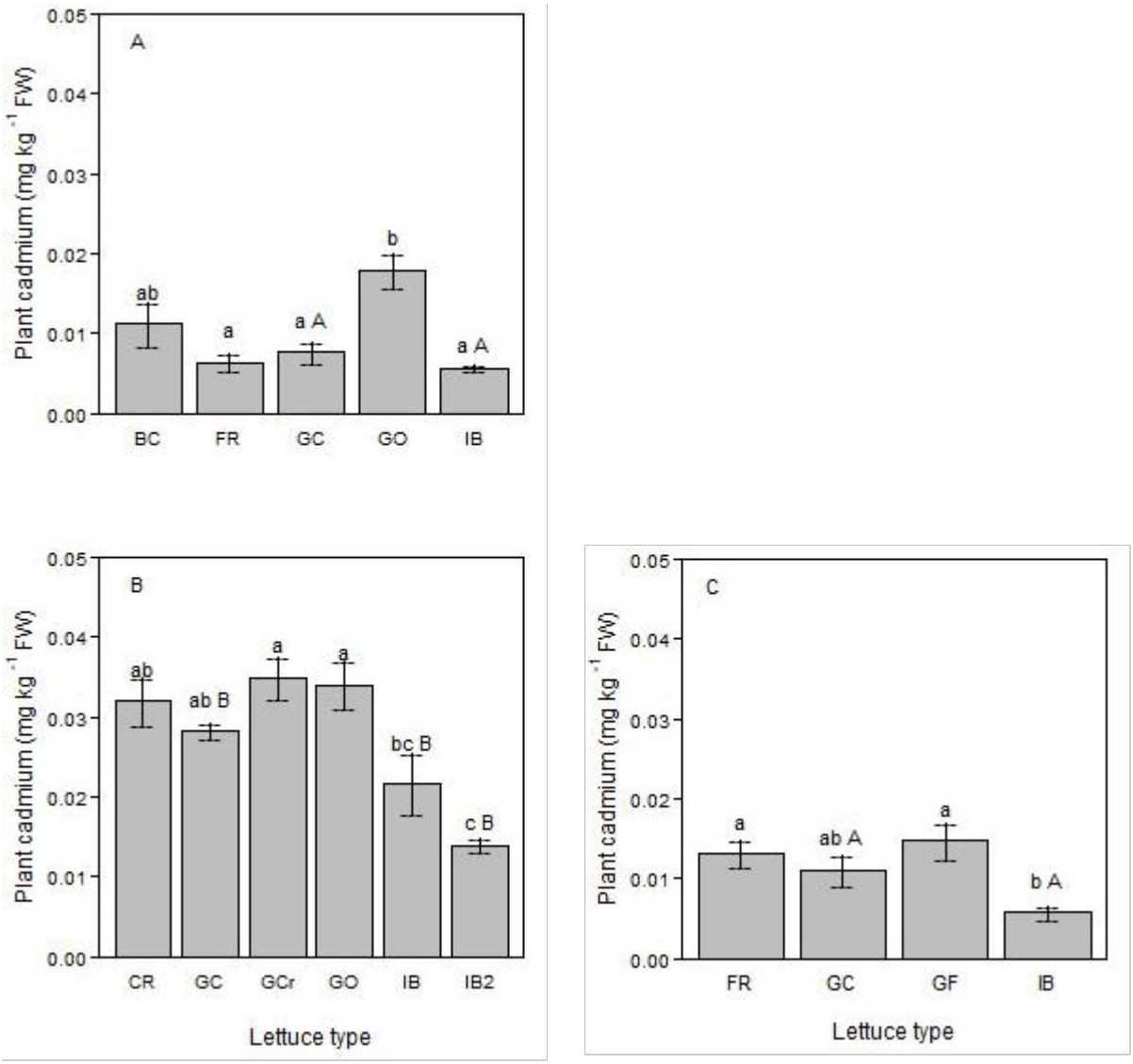

Figure 6.1 Cadmium concentration (mg kg^{-1}) of different lettuce varieties grown in (A) Pukekohe, (B) Gisborne and (C) Canterbury. Mean and standard error (n = 3) indicated by the same lower case letter are not significantly different ($P < 0.05$) within a given region. Note: IB and IB2 grown in Pukekohe and Gisborne were grown at different locations from the other lettuce types. Mean and standard error (n = 3) indicated by the same uppercase letter are not significantly different ($P < 0.05$) between regions for the same lettuce type.

Green Cos and Iceberg were the only lettuce grown in all three regions, with significantly higher Cd concentrations observed in lettuce grown in Gisborne compared to those grown in Pukekohe and Canterbury (Figure 6.1). Soil Cd concentrations were similarly low in Canterbury (site mean 0.12 mg kg^{-1}) and Gisborne (0.14–0.23 mg kg^{-1}), with Pukekohe having the highest concentrations (0.52–0.63 mg kg^{-1}) (Figure E3 in Appendix). Aggregating Cd concentrations from all lettuce samples shows plant

uptake of Cd was highest in Gisborne (median PUF: 3.6), followed by Canterbury (median PUF: 2.1), with the lowest uptake occurring in Pukekohe (median PUF: 0.45) (Figure E3).

General soil properties for the lettuce sites are shown in Table 6.2. The mean soil pH across all the sites was close to 7, with all sites except one (IB in Gisborne) having pH > 6. Lettuce (Iceberg) grown at this site had elevated Cd compared to Iceberg lettuce grown at a different site in Gisborne (IB2) with a pH of 6.7 and slightly lower soil Cd (0.15 vs 0.20 mg kg^{-1}).

Mean lettuce Cd concentrations were comparable to concentrations in lettuce from a recent total diet survey (0.4 mg kg^{-1} [DW] (Pearson et al. 2018) or 0.02 mg kg^{-1} [FW]), assuming 5% dry matter;) and Iceberg lettuce sold commercially in the Waikato region (mean: 0.019 mg kg^{-1}; *n* =11, range 0.004–0.042 mg kg^{-1}) (Kim 2005), and lower than in lettuce from Pukekohe market gardens (mean: 0.04 mg kg^{-1}; *n* = 30, range 0.01 – 0.14 mg kg^{-1}; (Roberts et al. 1995). Cd concentrations in all lettuce types were at the lower end of the range (0.001 – 0.24 mg kg^{-1}) reported in international studies (Baldantoni et al., 2016; Grybauskaite et al., 2014; Lin et al., 2015; Tang et al., 2016), and markedly below the Food Standard of Australia and New Zealand (FSANZ) ML for Cd in leafy greens of 0.1 mg kg^{-1}, and the Codex (CODEX, 2018) and European Commission (2006) MLs of 0.2 mg kg^{-1}.

Table 6.2 Summary of properties of sampled soils.

Soil property	Lettuce soils			Onion soils			Spinach soils		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
Total Cd (mg kg^{-1})	0.3	0.16	0.10–0.78	0.42	0.29	0.08–1.35	0.25	0.27	0.07–0.47
pH	6.7	6.7	5.4–7.7	6.2	6.2	5.9–7.8	6.6	6.6	5.6–7.6
Olsen P (mg kg^{-1})	108	113	44–178	41	41	20–70	90	81	30–205
Total P (mg kg^{-1})	1,530	1,160	951–2,690	1,990	1,660	694–4,390	1,645	1703	664–3376
Total C (%)	1.8	1.9	1.1–2.33	4.2	4.3	2.1–6.67	2.47	2.26	1.08–4.87
Total N (%)	1.3	1.01	0.55–2.55	0.39	0.42	0.17–0.64	0.24	0.23	0.08–0.51
K (cmolc·kg^{-1})	14.9	11.1	7.6–27.4	0.86	0.79	0.29–1.56	1.1	0.9	0.3–3.22
Ca (cmolc·kg^{-1})	2.3	1.6	0.78–3.89	9.91	9.6	7.4–12.8	12.8	11.9	5.1–22.9
Mg (cmolc·kg^{-1})	0.3	0.23	0.1–0.63	1.53	1.36	0.63–2.85	1.8	1.49	0.64–6.45
Na (cmolc·kg^{-1})	21.5	20	11–35	0.16	0.16	0.06–0.24	0.14	0.11	0.05–0.94
CEC (cmolc·kg^{-1})	0.2	0.15	0.08–0.23	20	20	14–26	18	19	9–27
Total Zn (mg kg^{-1})	92	86	68–138	108	115	73–141	92	92	53–188
*Total Cl (mg kg^{-1})	22.3	21	9.1–50	28.5	30.2	17.7–36.1	13.5	10.1	2.0–47.6
*Sand (%)	12	12	3–27	17	14	2–35	18	11	0–43
*Silt (%)	44	47	28–61	52	50	43–63	49	49	25–71
*Clay (%)	43	50	12–60	27	28	23–29	31	29	12–66

*Total chloride and soil texture determined from a single composite transect taken across the site.

6.3.2 Onions – effect of cultivar

Mean onion Cd concentration in the four cultivars ranged between 0.008 mg kg^{-1} and 0.044 mg kg^{-1} (*n* = 32), with an overall mean concentration of 0.018 mg kg^{-1} (Figure 6.2). This mean concentration is comparable to that in onions from a recent New Zealand total diet survey (0.2 mg kg^{-1} [DW] Pearson et al. 2018; 0.02 mg kg^{-1} [FW], assuming 10% dry matter), those sold commercially in the Waikato region (mean 0.016 mg kg^{-1}, range 0.003–0.068 mg kg^{-1}, *n* = 36; Kim 2005), and Pukekohe (0.02 mg kg^{-1}, range 0.01–0.11 mg kg^{-1}, *n* = 30; Roberts et al. 1995). New Zealand onion concentrations were at the lower end of the range reported in international studies (0.003 to 0.41 mg kg^{-1}) (Alexander et al., 2006; Bešter et al., 2013; Bystricka et al., 2016; Lin et al., 2015; Weeks et al., 2007), which were largely from residential gardens or pot trials. No ML is specified for bulb vegetables by FSANZ, although the mean concentration of Cd in the red onion from Pukekohe (RV1) was approaching the Codex and European MLs of 0.05 mg kg^{-1} (FW) (CODEX, 2018; European Commission, 2006).

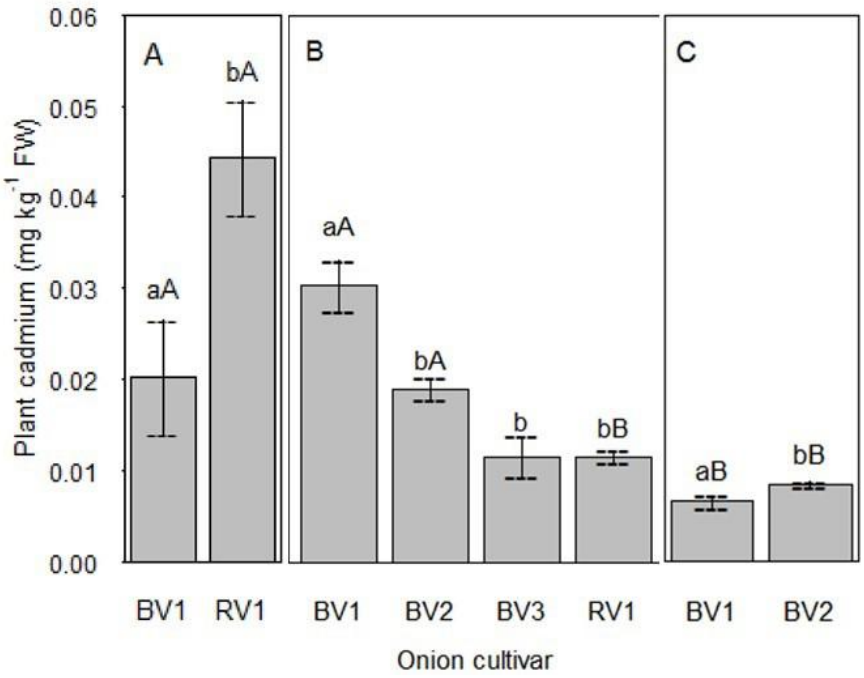

Figure 6.2 Cadmium concentration in onion cultivars (mg kg^{-1} FW) from (A) Pukekohe, (B) Waikato and (C) Canterbury. Mean (n = 4) and standard error indicated by the same lower case letter are not significantly different ($P < 0.05$) within a given site, or between sites (capital letters) for cultivars present at more than one site.

There were significant differences in onion Cd concentrations between cultivars, although these were not consistent across sites (Figure 6.2). Bystricka et al. (2016) found significant differences in onion Cd concentrations in six onion cultivars, with mean concentrations ranging between 0.022 and 0.04 mg kg^{-1} (FW), while Alexander et al. (2006) reported no difference in Cd uptake by six onion cultivars. The higher Cd concentration in the red onion from Pukekohe (RV1) may be attributable to the lower soil pH observed at this site compared to the other sites; soil carbon was also lower than most other sites (data not shown). Bešter et al. (2013) found that higher pH and organic matter reduced onion Cd concentrations. A more extensive comparison between Cd uptake and soil properties for this study is reported in the next section.

6.3.3 Field survey – soil properties

Mean concentrations of selected soil properties from the survey sites for onion and spinach are given in Table 6.2. Total soil Cd concentrations for the onion sites ranged between 0.08 and 1.35 mg kg^{-1}. The overall mean soil Cd concentration for the onion sites was 0.42 mg kg^{-1} (median 0.29 mg kg^{-1}), which is higher than the mean and median Cd for cropping soil of 0.28 mg kg^{-1} and 0.21 mg kg^{-1}, respectively (Cavanagh, 2014). Cadmium concentrations in Waikato and Pukekohe are higher than those in Canterbury and Hawke's Bay (Figure 6.3A), as observed in larger soil surveys (Cavanagh, 2014). The highest Cd concentrations in the Pukekohe region occurred in an organic soil, which had a low volume weight (surrogate for bulk density). Total soil Cd concentrations for the spinach sites ranged between 0.07 and 0.46 mg kg^{-1} (Figure 6.3B), with mean soil concentration of 0.25 mg kg^{-1} (median 0.26 mg kg^{-1}). Most onion samples (73%) and all spinach samples had soil Cd concentrations below the TFMS tier 1 trigger of 0.6 mg kg^{-1}. Other soil properties recognised as affecting plant uptake of Cd also varied, with soil pH ranging from low to high, while total C and CEC were low to medium (Blakemore et al., 1987). Soil type ranged from clay to silt loams.

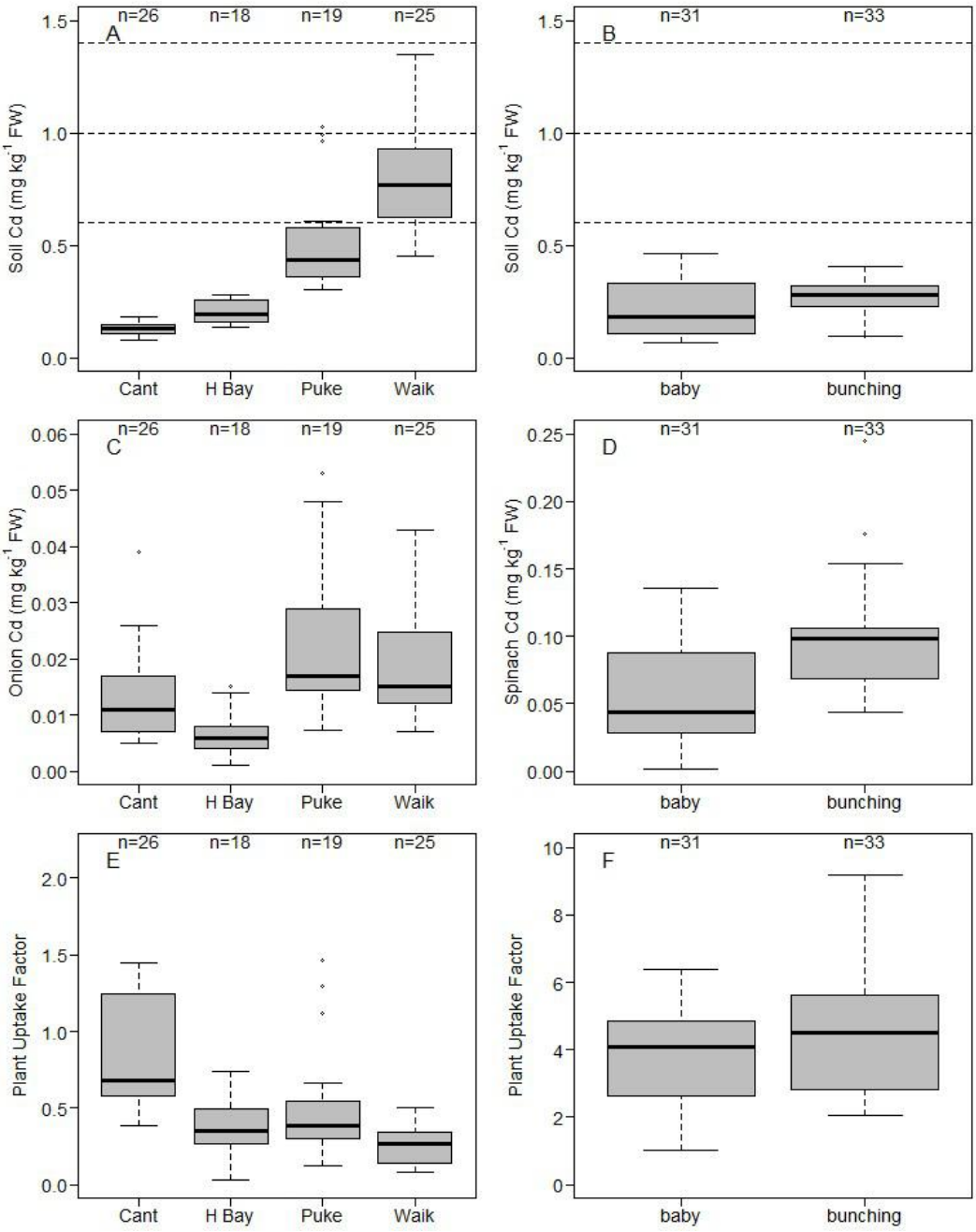

Figure 6.3 Total soil cadmium concentration (mg kg^{-1}) in each region (Cant = Canterbury, H Bay = Hawkes Bay, Puke = Pukekohe, Waik = Waikato) sampled for onions (A) or in soils sampled for baby and bunching spinach (B). The dashed line is the TFMS trigger value for Tiers 1, 2, and 3. Mean Cd concentrations (mg kg^{-1} FW) in onions from each region (C) and baby and bunching spinach (D). Plant Uptake Factor for each region for onions (E) or for baby and bunching spinach (F). Boxes depict the 25th and 75th percentile values, with horizontal lines plotted within boxes representing the median value. Whiskers show the 10th and 90th percentile values and outliers are represented by circles and are values that are > 1.5 times the interquartile range. n = individual plot samples, with three or four plots sampled per site.

6.3.4 Field survey – cadmium concentrations in onions and spinach

Mean onion Cd concentration ranged between 0.007 and 0.05 mg kg^{-1} (*n* = 88), with an overall mean concentration of 0.016 mg kg^{-1} (Figure 3C), similar to the cultivar study (Figure 6.2). There was significant regional variation in onion Cd concentrations (Figure 3C), with onions from Pukekohe, Waikato and Canterbury having significantly higher concentrations than those from Hawke's Bay (*P* < 0.05). Cadmium concentrations in onions from Pukekohe were significantly higher than those from Canterbury (*P* < 0.05), although there was no significant difference between Cd in onions from Canterbury and Waikato *(P* = 0.093). Plant uptake also varied between regions (Figure 3E), and was highest in Canterbury and similar across the other regions. One site (three replicate plots) in Pukekohe showed elevated plant uptake; this site had an unusually low mean pH of 5.4 when compared to the other sites in the region (mean pH ranging between 6.0 and 6.6), which may explain the discrepancy.

Mean spinach Cd concentrations ranged between 0.005 and 0.11 mg kg^{-1} for baby leaf spinach (*n* = 31), with an overall mean of 0.06 mg kg^{-1} (Figure 3D). Concentrations were generally higher in bunching spinach, and site mean concentrations ranged from 0.07 mg kg^{-1} to 0.19 mg kg^{-1}, with an overall mean concentration of 0.1 mg kg^{-1} (*n* = 33). The overall mean for both spinach stages was 0.08 mg kg^{-1}. Cadmium concentrations in spinach were at the lower end of the range (0.015 to 4.14 mg kg^{-1}) reported in international studies (Grybauskaite et al., 2014; Lin et al., 2015; Tack, 2014). The mean concentrations at a number of sites exceeded the FSANZ ML for Cd in leafy greens of 0.1 mg kg^{-1}, although they were less than the Codex (CODEX, 2018) and European Commission MLs of 0.2 mg kg^{-1} (European Commission, 2006).

The influence of harvest stage on Cd concentrations was assessed at two sites where baby leaf spinach, and subsequently bunching spinach from the same crop, was sampled. Bunching spinach had significantly higher concentrations than baby spinach, suggesting Cd continues to be accumulated over time and is not diluted with growth (Figure E3). Limited assessment of variation between cultivars was undertaken, with three cultivars tested at one site: two were grown at the same time, while a third was grown over winter and thus for a longer period. This cultivar had significantly elevated Cd compared to the other cultivars (Figure E3), which may be attributable to a longer growth period and/or cultivar variation.

A second baby-leaf spinach crop (P1b2) grown at P1 had significantly higher Cd compared to the first baby spinach crop (P1b1), although the reason for this difference is unclear. Tack (2017) observed significantly higher concentrations in spinach subjected to limited water supply during periods of

high demand, which may suggest water stress is a reason for the observed difference. However, further investigation, including of other crop management factors that have been shown to influence Cd uptake, such as fertiliser (N, micronutrients), is required (Larsson & Asp, 2011; Paul & Chaney, 2017).

6.3.5 Relationship between soil properties and cadmium uptake by onions and spinach

Soil Cd and pH were significant predictors of onion Cd concentrations, explaining 38% of the variation, while inclusion of region as an additional variable explained 50% of the variation (Table 6.3). Assessing the influence of a wider set of soil properties (and excluding region) also improved prediction, with soil Cd, CEC, and exchangeable Mg and Ca concentration explaining approximately 48% of the variability in onion Cd concentrations (Table 6.3), which may suggest it is differences in these variables that are leading to the observed influence of region.

Table 6.3 Soil–plant transfer relationships derived for onion and spinach

Crop	Equation	Adj-R^2
Onion	3) $\log Cd_{onion} = 1.079 + 0.572 \log(Cd_{soil}) - 0.271$ pH	0.38
	4) $\log Cd_{onion}$ = Region + $0.50519 \log(Cd_{soil}) - 0.2422$ pH Region [@] Canterbury = 0.933 Hawke's Bay = 0.652 Pukekohe = 0.947 Waikato = 0.888	0.5
	5) $\log Cd_{onion} = -1.365 + 0.481 \log(Cd_{soil}) + 1.60 \log(CEC) - 0.511 \log(Mg_{ex}) - 1.252 \log(Ca_{ex})$	0.48
Baby spinach	6) $\log Cd_{spin} = -0.138 + 0.2562 \log(Cd_{soil}) + 0.3875 \log(Mg_{ex})$	0.49
	7) $\log Cd_{spin} = 1.37 + 0.405 \log(Cd_{soil}) + 0.36 \log(Mg_{ex}) - 0.732 \log(Zn)$	0.55
Bunching spinach	8) $\log Cd_{spin} = 0.8022 + 0.8988 \log(Cd_{soil}) - 0.7958 \log(C)$	0.42

[@] The number next to each region is the constant value of the model.

Clay content and chloride were not significant predictors of Cd concentration. The low proportion of variation explained may be attributable to the relatively small range in Cd concentration (0.08 to 1.35 mg kg^{-1}) and other soil properties. For example, Bešter et al. (2013) found pH, soil Cd and organic C explained 85% of the variation in onion Cd concentrations. However, in their study the range of soil Cd concentrations (0.2 to 40 mg kg^{-1}) and organic matter (3.3% to 13.8%, or 1.9% C to 8% C), was much greater than in our study; moreover the Bešter et al. (2013) study was undertaken

over a much more limited geographical area, which we would expect to also constrain differences in plant uptake mainly to soil properties. Onion Cd concentrations predicted using the identified relationships (Equations 3 and 4 in Table 6.3) show that the models tend to under-predict onions with high Cd, compared with observed concentrations (Figure E4).

Soil Cd and exchangeable Mg were significant predictors of Cd concentration in baby spinach, explaining 49% of the variation in spinach Cd concentrations (Table 6.3). The inclusion of Zn increased the percentage of variation explained to 55%. While the influence of Zn on Cd uptake by plants is widely reported (e.g. Oliver et al., 1994; Sarwar et al., 2010), there are few studies that have examined the relationship between Cd and Mg, with studies generally reporting increased soil Mg concentrations lead to reduced Cd concentrations (Borišev et al., 2016; Kubo et al., 2008), whereas we observed the opposite. Further investigation is required to determine the significance of this finding. In bunching spinach, soil Cd and C were significant predictors of Cd concentrations, explaining 42% of the variation in spinach Cd concentrations (Table 6.3). Comparison of predicted Cd concentrations with observed concentrations showed no bias toward under- or over-prediction of either baby or bunching spinach Cd concentrations (Figure E4).

The low to moderate proportion of the variation in plant Cd explained by the derived soil–plant relationships suggests that factors other than those assessed (e.g. water management, fertiliser input, climate) are also influencing plant uptake. The poor explanatory power is also partly attributable to the relatively narrow soil Cd concentration range, particularly for spinach, and other soil properties (e.g. pH) that are typically managed to meet agronomic optimums for individual crops. As sampling was undertaken in the main growing areas of each crop, soil Cd concentrations are considered to be representative of the concentrations in which these crops are currently grown, and further sampling within these regions is unlikely to extend the concentration range.

6.3.6 Implications for managing Cd uptake in leafy greens and onions to meet regulatory maximum levels

Cadmium concentrations in all lettuce types assessed in this study were markedly below the FSANZ ML. The inclusion of regions where plant uptake of Cd was comparatively high, thereby posing greater risk of elevated plant Cd, suggests there is minimal risk of Cd concentrations in lettuce exceeding regulatory standards. Therefore the requirement for active management of Cd in lettuce crops is low. This is also reflected in the estimates of soil Cd concentrations above which food standards might be exceeded (nCdFS) for individual sites, which were markedly above current soil Cd concentrations measured in this study for the individual regions (Tables 6.4 & 6.5).

Table 6.4 Soil cadmium concentrations at which EU maximum levels for onions (0.05 mg kg^{-1} FW) and FSANZ maximum levels for leafy greens (0.1 mg kg^{-1} FW) are predicted to be met (nCdFS), as a function of soil properties.

Soil pH	Onions nCdFS (mg kg^{-1}) National average	Canterbury	Hawkes Bay	Pukekohe	Waikato	Spinach soil C	Spinach nCdFS (mg kg^{-1})
5.5	1.7	1.6	5.6	1.5	1.9	2	0.24
6	2	2.7	9.8	2.5	3.3	3.5	0.36
6.5	2.2	4.7	17.0	4.4	5.8	5	0.48

Table 6.5 Soil Cd concentrations (mean and 95th percentile range) at which EU maximum levels for onions (0.05 mg kg^{-1} FW) and FSANZ maximum levels for leafy greens (0.1 mg kg^{-1} FW) are predicted to be met (nCdFS), based on observed plant uptake in different regions.

Region	nCdFS (mg kg^{-1}) Onion	Lettuce	Spinach (all regions*)
Pukekohe	1.43 (0.38–2.94)	5.6 (2.7–8.2)	
Waikato	2.54 (1.05–5.0)		0.35 baby leaf (0.14–0.7)
Gisborne		0.7 (0.45–1.1)	
Hawke's Bay	2.32 (0.80–5.7)		0.29 bunching spinach (0.2–0.44)
Canterbury	0.72 (0.35–1.24)	1.2 (0.65–1.9)	

* Regional estimates were not made as samples were from a limited number of sites within each region.

A small number of onion samples had Cd concentrations close to or above the European Commission (2006) ML of 0.05 mg kg^{-1}, and sites with elevated onion Cd concentrations often had a soil pH below 6. However, the nCdFS derived on the basis of the identified soil–plant relationships (Equations 3 and 4), including at a pH of 5.5, were markedly above current soil Cd concentrations. This suggests caution in the use of these values, and relationships, as triggers for managing compliance with regulatory food standards. The nCdFS, derived from the PUF perhaps provides a better reflection of the Cd concentrations to indicate the risk of non-compliance and highlights the variability that can occur across individual sites.

From a practical perspective, maintaining soil pH at or above 6 may be sufficient to ensure that Cd concentrations in the onion cultivar assessed in this study comply with relevant MLs. However,

further testing of onions and soil, including additional cultivars, is required to determine the wider applicability of this observation. Similarly, further research could be undertaken to determine if plant management practices (such as irrigation, fertiliser type and rates, and amendment addition) affect Cd uptake, and could explain a greater proportion of the variation in onion Cd concentrations.

The comparatively high Cd concentrations in baby and bunching spinach (close to or above the FSANZ ML of 0.1 mg kg^{-1} [FW]) suggest that management actions should be undertaken to reduce Cd uptake. The nCd_{FS} derived using soil–plant relationships and PUF similarly identify that current soil Cd concentrations present a risk of non-compliance. As soil pH is typically managed to around 7 for spinach crops, adding lime offers limited value for reducing Cd uptake in spinach. Further, spinach from a number of sites with a pH close to 7 were close to or exceeded the ML.

Given the significant relationship between Cd concentrations in bunching spinach and soil C, compost addition may help to reduce Cd uptake. However, field trials are required to establish the extent to which Cd concentration in bunching spinach is reduced. Some greenhouse trials have shown that adding municipal compost or manure to soil can reduce Cd uptake by spinach (Al Mamun et al., 2016; Kumarpandit et al., 2017), while others found that the reduction in pH following biosolids compost addition negated the Cd binding by the compost (Paul & Chaney, 2017). The latter study highlighted the importance of pH management, along with Zn supplementation, to minimize Cd uptake by spinach. Other management factors such as the watering regime (Tack, 2017), and nitrogenous fertilisers may also influence Cd uptake (Larsson & Asp, 2011). Further research on the influence of crop management practices, in particular water management but also N fertiliser and trace element application (e.g. Zn), on Cd uptake by spinach is required to determine the extent to which these practices can also be implemented to lower Cd uptake.

Finally, we note that the EU ML for spinach is double that of the FSANZ ML (0.2 mg kg^{-1} [FW] vs 0.1 mg kg^{-1} [FW]). As the standards are established on the basis of being as low as reasonably achievable while ensuring protection of human health, it may be relevant to review the FSANZ ML for spinach to determine whether this principle is being met.

Soil Cd concentrations are often the primary focus for managing Cd uptake in food crops with soil–plant transfer models indicating key soil variables that influence Cd uptake and used to develop risk-based soil guideline values as a function of soil properties (e.g. de Vries & McLaughlin, 2013; Junhe et al., 2017). Such values have successfully been used by farmers in the border area of the Netherlands and Belgium, resulting in trust between supermarkets, food companies, and regulators (Smolders et al., 2007). Our derived values are similar to those derived by Smolders et al. (2007) for

onions and spinach, although are much higher for lettuce. However, the relatively low proportion of variation in plant Cd explained by our derived soil–plant relationships limits their application for this purpose. The wide range of nCdFS values derived using PUF highlights the variation that can exist between sites, and the challenge in applying generic Cd soil guideline values without considering other soil properties, even if developed for a specific crop and region. Equal weight should be placed on managing other soil properties, in particular pH and C, to ensure these are also at an optimum for minimising Cd uptake. Further, we suggest that crop management factors, in particular water management, may play a greater role in determining Cd uptake than previously thought, especially where relatively high plant Cd concentrations are observed in crops grown in soils with comparatively low soil Cd concentrations.

6.4 Conclusions

Cadmium concentrations in a range of lettuce types and cultivars were more than tenfold lower than the FSANZ ML of 0.1 mg kg^{-1} (FW), with the lowest Cd concentrations consistently occurring in Iceberg lettuce. Cadmium concentrations in onions varied between sites, and mean concentrations (0.016 mg kg^{-1} FW) were well below the Codex and EC MLs of 0.05 mg kg^{-1}(FW). The highest Cd concentrations were observed in spinach, with concentrations in baby leaf and bunching spinach approaching or exceeding the FSANZ ML of 0.1 mg kg^{-1} (FW) at a number of sites, although they were below the Codex and EU MLs of 0.2 mg kg^{-1} (FW).

In addition to soil Cd concentrations, pH was a significant factor influencing Cd uptake in onions, and exchangeable Mg or C significantly influenced Cd concentrations in baby leaf and bunching spinach, respectively. The identification of pH and C as significant factors influencing Cd uptake in onion and bunching spinach, respectively, indicates management of these properties may help to minimise Cd uptake in those crops.

Soil–plant relationships identified for onions and spinach explained a low to moderate proportion of the variation, creating a low confidence in risk-based soil guideline values determined from these relationships. This is particularly the case for onions, for which the soil–plant relationship under-predicted elevated onion Cd concentrations. This low to moderate proportion of explained variation is partly attributable to the narrow range in some measured soil properties, but also suggests that factors other than those assessed are influencing plant uptake. More comprehensive research is required to determine the extent to which plant management practices such as water management or fertiliser type (especially micronutrients) and rates affect Cd uptake in these crops.

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Chapter 7

Cadmium concentrations in New Zealand wheat: Effect of cultivar type, soil properties, and crop management

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My contribution to this article: I completed most of the laboratory work on soil and plant sample analysis. I collated the data from the field survey samples and contributed to discussions for the writing of this manuscript.

7.1 Introduction

Cadmium (Cd) is an environmental soil pollutant that occurs naturally at trace levels in soils, but is also an incidental impurity in many phosphate (P) fertilisers. Soil Cd is readily absorbed by plants and therefore can enter the human food chain through the crops and crop based products we consume in our diet (Clemens et al., 2013; Rietra et al., 2017; Song et al., 2017). Chronic exposure to Cd above acceptable levels may pose a threat to human health, through its toxicity to the renal cortex, and adverse effects on the cardiovascular, pulmonary and musculoskeletal systems (Järup & Åkesson, 2009).

Along with crops such as rice (*Oryza saliva L.*) and potatoes (*Solanum tuberosum L.*), wheat (*Triticum aestivum L.*) is an inadvertently important source of dietary Cd in humans in several regions of the world, as it is used in bread and pasta (Fan et al., 2009; Rietra et al., 2017). Food standards have been set to provide for a safe level of Cd intake over a lifetime. While an occasional exceedance presents a low health risk, it could present trade or reputational risk to a country. It is therefore important that Cd uptake in wheat grain is maintained below the maximum acceptable standard set by regulatory bodies. To help manage Cd uptake, research has focused on trying to identify factors that affect Cd uptake in wheat. Broadly, these can be summarised into soil, plant and crop management factors (Grant et al., 2008; Rizwan et al., 2017). The most important soil factors found to affect Cd uptake in wheat include soil pH value (Eriksson, 1990; Oliver et al., 1996), soil organic

matter content (Wenzel et al., 1996), soil salinity concentration (Forster et al., 2018; Norvell et al., 2000), total soil Cd concentration (Adams et al., 2004) and soil zinc (Zn) concentrations (Oliver et al., 1994). Plant factors, such as wheat cultivar type have been reported as having a large effect on wheat grain Cd concentrations (Adams et al., 2004; Gray et al., 2002; Perilli et al., 2010). A range of crop management practices have also been shown to affect Cd uptake in wheat grain. Some of these include the rate, type and timing of nitrogen (N) and P fertiliser application (Gao & Grant, 2012; Grant et al., 2008; Ishikawa et al., 2015), timing of seeding (Perilli et al., 2010), crop rotation sequence (Oliver et al., 1993), type of tillage (Gao & Grant, 2012), application of Zn fertilisers (Forster et al., 2018) and irrigation (Gray et al., 2002).

Wheat is a staple food in New Zealand and like many other countries a contributory source of Cd in the diet (Pearson et al., 2018). However, only three field studies have measured Cd uptake in wheat in New Zealand (e.g. Gray et al., 2001; Gray et al., 2002; Roberts et al., 1995). These were restricted in their geographical distribution, and given they were all undertaken at least 18 years ago, many of the wheat cultivars are no longer commercially grown. The limited information on Cd uptake in wheat cultivars currently grown and the limited information on the effects of soil properties, cultivar type and crop management on Cd uptake in wheat across the main growing areas in New Zealand, seriously constrains our ability to determine if Cd concentrations in wheat are currently compliant with the maximum limit (ML) of 0.1 mg kg^{-1} FW, and what factors affect Cd uptake and could be exploited to minimise Cd uptake in wheat.

To address the concerns of the gradual accumulation of Cd in New Zealand soils, a Cadmium Management Strategy (CMS) was implemented in 2011 to ensure that 'Cd in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years' (MAF, 2011). Central to the strategy is a Tiered Fertiliser Management System (TFMS), which contains five tiers and four trigger concentrations, whereby as soil Cd concentrations increase, increasingly stringent fertiliser management practices are imposed. The trigger values in the TFMS are however considered only interim because there was little New Zealand-specific Cd data available at the time to inform their development (Warne, 2011). It is therefore unknown to what extent the trigger values are protecting ecological receptors, soil health and food quality (Cavanagh, 2013).

There have been occasional exceedances of our food standards for Cd in wheat grain at soil Cd concentrations well below the lowest soil trigger value of 0.6 mg kg^{-1} (Gray et al., 2001), suggesting the trigger values currently in the TFMS may not be sufficiently consistent with the objectives outlined in the CMS for some regions of New Zealand.

The objectives of this study were i) to explore the plant factor by measuring Cd concentrations in 12 commercial wheat cultivars, and ii) to explore the relationships between soil, plant and crop management factors by determining Cd uptake in two commercial wheat cultivars growing in all the major commercial growing regions of the country. This study is part of a larger body of research that is assessing Cd uptake in other crops (e.g. potatoes, onions, lettuce and spinach) that collectively can then be used to inform the future development of New Zealand-specific risk-based trigger values.

7.2 Methods and methods

7.2.1 Sites and sampling

Soil and wheat plant samples were collected from a combination of industry and commercial field sites. In 2015, Cd concentrations were determined in 12 wheat cultivars grown across three sites: Methven (NZTM 1494165E 5168752N), Temuka (NZTM 1468593E 5101956N) and Oreti (NZTM 12474018E 4869877N), all located on New Zealand's South Island. This included bread, biscuit and feed wheat cultivars. In 2016-17, Cd concentrations were determined in two wheat cultivars, Reliance (bread) and Empress (biscuit), grown across 34 sites, with sites in both the North (6 sites) and South (28 Sites) Islands. Sampling details are summarised in Table 7.1.

7.2.2 Crop management information

Crop management information was obtained from the trial operators or where possible from a questionnaire supplied to the farmer. Information supplied included dry matter yield, irrigation, rates and types of fertiliser and pesticide applied.

7.2.3 Soil and plant analysis

Soils were oven-dried (35 °C) until a constant weight and sieved (<2 mm) before analysis. Soil pH was determined in a 1:2 soil: water solution by potentiometric analysis (Blakemore et al. 1987). Exchangeable potassium (K), calcium (Ca), magnesium (Mg) and sodium (Na) were measured in a 1 M neutral ammonium acetate extract (Blakemore et al., 1987), and analysed by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES). Cation exchange capacity (CEC) was calculated by summing concentrations of extractable cations and extractable acidity. Bioavailable P (Olsen P) was determined by bicarbonate extraction (Olsen, 1954). Total carbon (C) and nitrogen (N) were determined by combustion using an Elementar Vario-Max CN Elemental analyser. Soil chloride concentrations were measured in a filtered 1:5 soil: water extract by ion chromatography. Pseudo total concentrations of Cd, zinc (Zn), P, aluminium (Al) and iron (Fe) were determined by microwave

digestion using nitric acid and hydrogen peroxide as reported by Simmler et al. (2013); these will be referred to forthwith as total concentrations for simplicity. The digests were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for Cd and ICP-OES for Zn, P, Al and Fe. Particle size analysis was measured using the pipette method (Claydon, 1989).

Wheat grain and straw samples were weighed, dried at 60°C to a constant weight, and weighed again to enable reporting of data on a fresh weight (FW) and dry weight (DW) basis. Whole wheat grain and straw samples were ground and digested using the nitric acid and hydrogen peroxide microwave digestion method described by Cindrić et al. (2015). The digests were analysed for Cd by ICP-MS. In a selection of wheat grain samples, bran and the endosperm were separated from the whole grain and analysed for Cd by ICP-MS.

Table 7.1 Summary of sites and details of soil and plant sampling.

Year	Sites	Location	No. of cultivars	Sampling details
Wheat cultivar study				
2015	3 industry trial sites	Methven (SI) Temuka (SI) Oreti (SI)	8 6 6	Wheat cultivars were grown in 4 replicate plots (1.5 × 12 m) arranged in a randomised block design. Soil and plant sampling were undertaken at harvest. For each plot, 5 soil cores (150 mm depth) were collected and combined to form a single composite soil sample. Bulk subsamples of wheat grain from each plot along with straw were provided by the grower. In addition a composite soil sample (150 mm depth) was taken along a 100 m transect.
Wheat survey				
2016 – 2017	34 samples from 28 industry trial and commercial sites	Canterbury (SI) Manawatū (NI) Hawkes Bay (NI) Southland (SI)	2	Reliance and Empress wheat cultivars were grown in 3 or 4 replicate plots as described above. At each commercial site, 3 plots (1 m × 1 m) were established randomly across a field. Within each plot, 100 heads of wheat were sampled and 5 soil cores (150 mm depth) were collected and combined to form a single composite soil sample. In addition a composite soil sample (150 mm depth) was taken along a 100 m transect.

The location in New Zealand is indicated by NI for North Island and SI for South Island.

7.2.4 Quality control/assurance

Soil and plant samples were digested in batches of up to 40. Each batch included at least one digestion blank. One out of every 20 samples was analysed in duplicate to confirm repeatability of the analysis. Cadmium concentrations in procedural blanks were used to calculate the method detection limits. Duplicate analysis of samples were within 5% of each other. The accuracy of soil and plant analysis was assessed using several internal and external certified reference materials including for soil (NIST Montana 2711; Interlab internal WEPAL soil 921; Interlab internal WEPAL soil 981), and plant (NIST 1573a, tomato leaves; ASPAC internal clover; ASPAC internal beetroot). Analytical results were within 5% of the certified values. The method detection limits for soil Cd were 0.020 mg kg^{-1} and 0.005 mg kg^{-1} in plant material.

7.2.5 Statistics

Grain and straw Cd data were subjected to Analysis of Variance (ANOVA) and data checked for normality by assessing residual plots. The data was not required to be transformed and effects were considered significant if they differed at the probability level of 5% based on Fisher's un-protected least significant difference (LSD) test. Relationships between grain Cd concentration and soil and plant variables from the paired soil and grain samples from the survey were estimated by linear and multiple linear regression analysis. Statistical analyses were performed by GENSTAT for Windows v18.

7.3 Results and discussion

7.3.1 Effect of cultivar type

Wheat grain Cd concentrations in cultivars ranged between 0.040 and 0.097 mg kg^{-1} FW (n=120) (Table 7.2), with a mean of 0.063 mg kg^{-1} FW (0.071 mg kg^{-1} DW). The mean concentration is higher than previously found in a larger survey (0.054 mg kg^{-1} FW) of Cd in wheat grain in New Zealand by Gray et al. (2001), although lower (0.072 mg kg^{-1} FW) than Roberts et al. (1995). Wheat grain Cd concentrations were at the upper end of the range of values (0.005 – 0.069 mg kg^{-1} FW) reported in several overseas surveys (Adams et al., 2004; Mench et al., 1997; Song et al., 2017; Wolnik et al., 1983). The mean concentration is lower than the Food Standards of Australia and New Zealand (FSANZ 2013) standard 1.4.1 ML for Cd in wheat of 0.1 mg kg^{-1} FW and the Codex Standard 193-1995 (Codex Alimentarius Commission (CAC), 2009) and European food standards of 0.2 mg kg^{-1} FW (European Commission, 2006). Although, two cultivars (Reliance and Conquest at the Methven site) had individual plot replicates that exceeded 0.1 mg kg^{-1} FW.

Table 7.2 Wheat type (Bi = biscuit; F = feed; Br = bread) and wheat grain Cd concentrations (mg kg^{-1} FW) in different cultivars at Methven, Temuka and Oreti sites. Mean (n = 4) and standard error followed by the same lowercase letter within a site are not significantly different ($P < 0.05$) or not significantly different between sites (capital letters).

Cultivar	Wheat type	Methven	Temuka	Oreti
Claire	Bi	0.059 (0.003) abA	0.040 (0.003) aB	0.059 (0.005) aA
KWM31	Br	0.063 (0.004) bc		
Phoenix	F	0.070 (0.004) cA	0.056 (0.004) bB	0.075 (0.009) aA
Raffles	Br	0.051 (0.002) a		
Reliance	Br	0.086 (0.006) d		
Sage	Br	0.052 (0.002) ab		
Saracen	Br	0.068 (0.005) c		
Conquest	Br	0.088 (0.006) d		
KWW47	Bi		0.049 (0.003) ab	0.069 (0.008) a
Empress	Bi		0.042 (0.002) a	0.062 (0.005) a
Wakanui	F		0.049 (0.003) ab	0.097 (0.010) b
Torch	F		0.056 (0.004) b	0.066 (0.002) a

There were significant differences in grain Cd concentrations between cultivars at all three sites (Table 7.2). Differences were greatest at Oreti where concentrations ranged from 0.059 to 0.097 mg kg^{-1} FW, compared to Temuka where concentrations only ranged from 0.040 to 0.056 mg kg^{-1} FW. Several investigations have previously reported variation in Cd concentrations in grain in different wheat cultivars (Adams et al., 2004; Gray et al., 2001; Perrier et al., 2016; Vergine et al., 2017), although the variation has generally been greater than that found in the present study. A survey in Japan reported more than a five-fold variation in wheat grain Cd concentrations between 237 wheat varieties (Kubo et al., 2008). Variation in the partitioning of Cd between plant organs (grain, roots, straw and leaves) rather than differences in total plant uptake of Cd are often cited as the main reason for the variation in grain accumulation between wheat cultivars (Greger & Löfstedt, 2004; Harris & Taylor, 2013), although differences in Cd uptake by roots between cultivars may be important (Kubo et al., 2016; Perrier et al., 2016). This natural variation in Cd uptake highlights the potential to use low Cd accumulating cultivars at sites where there is high Cd uptake, as well as breeding for low Cd accumulating cultivars (Clemens et al., 2013).

Wheat cultivars are bred for specific end uses (i.e. bread, biscuit, and feed wheat). Three of the 12 cultivars analysed were feed wheat (Phoenix, Wakanui and Torch), three biscuit wheat (Claire, KWW47 and Empress) and the remainder bread wheat. There is no evidence to indicate that Cd uptake in grain was overall higher in one type of wheat than another (Table 7.2). Furthermore, none

of the feed wheat samples had Cd concentrations that exceeded the maximum Cd limit (in the absence of a NZ standard) set in the European Union Animal Feed Directive 2005/87/EC (European Commission, 2005). This directive specifies a maximum limit of 1 mg kg^{-1} (based on a moisture content of 12%) for animal feed derived from vegetable origin which equates to a Cd concentration of 1.14 mg kg^{-1} DW.

In a subset of samples, the bran and the endosperm (*viz*. flour) were separated from the kernel and Cd was analysed in both fractions. Results showed that in all instances wheat Cd concentrations were higher (approximately two-four-fold) in the wheat bran than the flour (Figure 7.1). In addition, it appears that feed wheat (i.e. Phoenix and Wakanui) have proportionally higher amounts of Cd in their bran than the other wheat type cultivars. Compared to the European Commission (2006) food standard of 0.2 mg kg^{-1} for Cd in bran, four of the cultivars tested exceeded the standard. However, while bran has a higher Cd concentration, the wheat endosperm constitutes over 80% of the wheat grain (Mugford & Steele, 1980). Therefore, although the bran component of a wheat kernel contains higher Cd concentrations than the endosperm, it typically is a smaller contribution of Cd to the whole kernel. For example, Chaudri et al. (1996) found on average white flour contained 31% less Cd than wholemeal flour. Therefore, assuming the bran and the endosperm comprise approximately 20% and 80% of the whole grain respectively, preliminary findings in this study, would suggest that the bran component in grain may contribute between 33 and 52% of the whole grain Cd concentration depending on the wheat cultivar, potentially higher than previously reported.

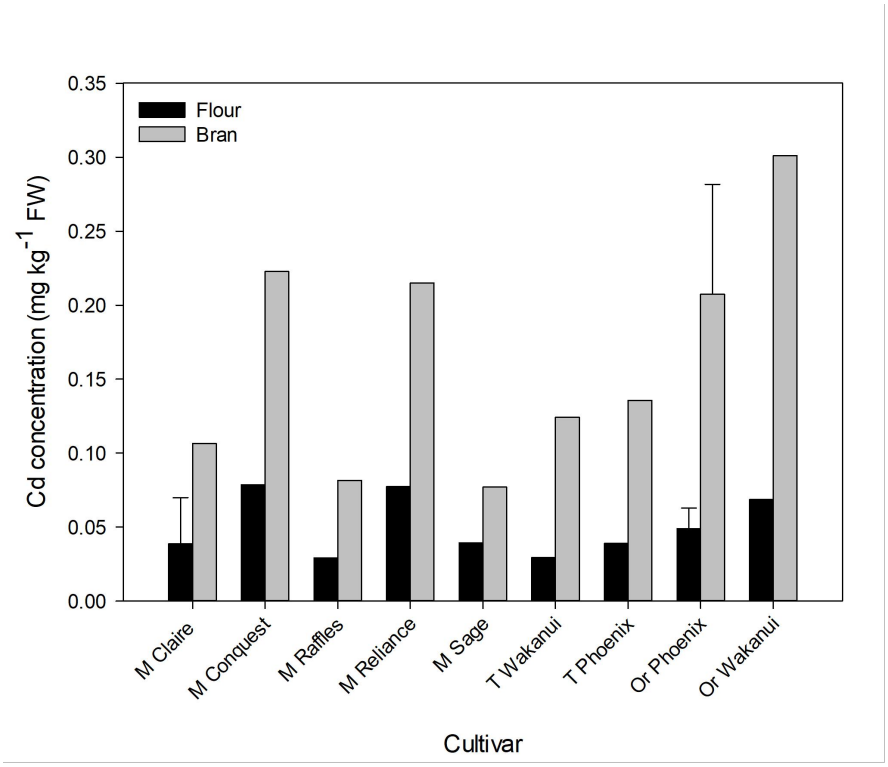

Figure 7.1 Comparison of Cd concentrations (mg kg^{-1} FW) in the wheat flour or bran in selected cultivars from the three trial sites Methven (M), Temuka (T) and Oreti (Or). Results are for single plot replicates, except for the cultivar Claire from Methven and Phoenix from Oreti which are the mean and standard deviation of two replicates.

Cadmium concentrations in straw samples ranged between 0.01 to 0.22 mg kg^{-1} FW (Supplementary Figure F7.1a, b, c in Appendix). Wheat straw in all instances contained higher Cd concentrations than did wheat grain. This is consistent with previous studies (Gray et al., 1999c; Öborn et al., 1995). It appears that while Cd is readily translocated and accumulates in the aerial parts of plants, it doesn't accumulate to the same extent in the fruiting bodies of the plant. Wheat straw is often baled and used as animal feed. When corrected for moisture, Cd concentrations in straw ranged from 0.08 to 0.30 mg kg^{-1} DW, well below the European limit (European Commission, 2005).

A comparison of Cd concentrations in two cultivars (Claire and Phoenix) grown at all three sites showed that for both cultivars there was no significant difference in grain Cd concentrations grown at either the Methven or Oreti sites (Table 7.2). In comparison, Cd concentrations in both cultivars at the Temuka site were significantly lower. In general, Cd concentrations in wheat were not consistent with soil properties. For instance, Cd concentrations were lowest at the Temuka site despite having the highest total soil Cd concentration (0.24 mg kg^{-1}), along with the lowest clay (20 %) and total C

content (2.5%), the combination of these factors has been known to increase Cd availability in soils (Garcia-Miragaya & Page, 1978; Kim & Fergusson, 1992). As indicated, Harris and Taylor (2013) propose that differences in root-to-shoot and xylem-to-phloem transfer of Cd play a key role in determining differences in Cd translocation between cultivars. It is possible these factors were more important than the measured soil properties in affecting Cd uptake. In addition, is possible site specific management (e.g. type, timing and amount of fertiliser and irrigation applied) had some effect on Cd concentrations in wheat between the sites. A more comprehensive comparison and discussion of soil and management factors affecting Cd concentrations in wheat grain from a larger number of sites is given in the next section.

7.3.2 Relationship between soil properties and Cd concentrations in wheat

Soil properties

Mean values of selected soil properties from the survey sites are given in Table 7.3. Total soil Cd concentrations ranged between 0.02 and 0.39 mg kg^{-1}, with a mean concentration of 0.15 mg kg^{-1}, half the mean concentration of 0.28 mg kg^{-1} reported for cropping soils in New Zealand (Cavanagh, 2014). Total soil Cd was correlated to total soil P (r = 0.50; P <0.001), although the relationship was weak compared to previous studies (Gray et al., 2001; Stafford et al., 2018c). Other soil properties recognised as affecting plant uptake of Cd also varied, with soil pH ranging between low to high, while total C and CEC were low to medium (Blakemore et al., 1987). The majority of soils were classified as silt loams.

Table 7.3 Selected soil properties (n = 129) from the survey sites (0 – 15 cm)

Soil property	Mean	Median	Min	Max
pH	5.9	6.0	4.7	6.8
Olsen P (mg kg^{-1})	27	24	9	77
Total P (mg kg^{-1})	984	986	463	1682
Total C (%)	2.70	2.62	1.35	4.33
Total N (%)	0.25	0.25	0.13	0.39
K $cmol_c kg^{-1}$	0.31	0.27	0.10	1.19
Ca $cmol_c kg^{-1}$	9.1	9.1	3.9	14.7
Mg $cmol_c kg^{-1}$	0.72	0.57	0.22	4.24
Na $cmol_c kg^{-1}$	0.13	0.10	0.04	0.67
CEC $cmol_c kg^{-1}$	16	16	9	22
Total Cd (mg kg^{-1})	0.15	0.15	0.02	0.39
Total Zn (mg kg^{-1})	73	72	34	129
*Extractable Cl (mg kg^{-1})	24	23	10	45
*Sand (%)	18	16	6	50
*Silt (%)	57	58	39	71
*Clay (%)	25	24	11	37

*Extractable Cl and soil texture determined using a single composite transect across the site.

Cadmium concentrations on wheat grain

Wheat grain Cd concentrations ranged between 0.004 and 0.205 mg kg^{-1} FW, with an overall mean concentration of 0.067 mg kg^{-1} FW (0.074 mg kg^{-1} DW) (Table 7.4). Consistent with the results in the cultivar study, grain Cd concentrations across all sites were significantly ($P < 0.05$) higher in the Reliance cultivar (0.073 mg kg^{-1} FW) than Empress (0.053 mg kg^{-1} FW). Most samples had grain Cd concentrations in the range between 0.050 and 0.075 mg kg^{-1} FW (Supplementary Figure F2 in Appendix), although 11 samples exceeded the ML for Cd in wheat. The non-compliant samples were all the Reliance cultivar planted in autumn, with the exception of one spring sample (Table 7.4).

Table 7.4 Wheat grain Cd concentrations (mg kg^{-1} FW) in cultivars Empress and Reliance. Mean followed by the same lowercase letter are not significantly different ($P < 0.05$) or not different between cultivar (capital letter).

Cultivar	Planted season	Irrigation	Number	Mean	Min	Max	SEM
Empress	Autumn	Non-irrigated	16	0.058a	0.026	0.087	0.003
		Irrigated	20	0.054a	0.013	0.092	0.005
	Spring	Non-irrigated	0	NA	NA	NA	NA
		Irrigated	3	0.022b	0.004	0.033	0.009
	Overall		39	0.053A	0.004	0.092	0.003
Reliance	Autumn	Non-irrigated	10	0.129c	0.073	0.205	0.016
		Irrigated	35	0.067a	0.032	0.107	0.003
		unknown	24	0.066a	0.013	0.161	0.007
	Spring	Non-irrigated	4	0.068a	0.055	0.081	0.006
		Irrigated	11	0.061a	0.024	0.096	0.007
		unknown	6	0.073a	0.052	0.120	0.010
	Overall		90	0.073B	0.013	0.205	0.004

NA not available

Single linear regression analysis between wheat grain Cd concentrations and soil properties (and grain yield) indicated the only significant relationships were with exchangeable Mg, Na, extractable Cl and silt content (Table 7.5). Of those Cl was negatively related to grain Cd concentration, which is opposite to what has been previously reported where elevated Cl have been shown to enhance Cd in plants (McLaughlin et al., 1994). In the present study the average soil Cl concentrations were an order of magnitude lower than those reported by McLaughlin et al. (1994). There was also a negative relationship between Na and Mg and grain Cd concentrations which has not been previously reported for wheat. Studies in other plant species have reported that Mg deficiencies can lead to increased uptake of Cd (Kudo et al., 2015), however given the soil Mg concentrations in the present study are adequate, it is unlikely this was important. Multiple linear regression identified no additional relationships.

Table 7.5 Relationships between soil properties and grain Cd concentration (mg kg^{-1} FW).

Regression equation		R^2	*P* value
Wheat grain Cd concentration	= 0.0812 – 0.0193 (Mg)	0.13	<0.001
	= 0.0803 – 0.1020 (Na)	0.08	<0.001
	= 0.1024 – 0.0014 (Cl)	0.15	<0.001
	= 0.0228 – 0.0008 (Silt)	0.04	<0.022

When data was analysed separately for relationships between each cultivar, planted in either autumn or spring, with or without irrigation and grain Cd concentrations, a limited number of improved relationships were found, however they were sometimes opposite to what has previously been reported and often contradictory. For example, CEC was both positively and negatively related to grain Cd concentrations (data not shown). The exception was total C which was negatively related to grain Cd concentration in autumn planted wheat for both cultivars, which is a soil property previously reported to be important for Cd sorption and reducing availability in soils (He & Singh, 1994; Kim & Fergusson, 1992).

7.3.3 Relationship between management factors and Cd concentrations in wheat

It is uncertain why there were no significant relationships between soil properties such as pH or total Cd, which have been previously shown to be important for Cd uptake in wheat, although the absence of relationships is not unique to this study (Gray et al., 2001; Mench et al., 1997). It may simply be that compared to studies that have reported relationships (Adams et al., 2004; Liu et al., 2015), soil properties in the current study are a lot narrower in range. It is also possible that site specific management had some effect on Cd uptake between sites. Another factor which has not been extensively explored is the depth at which wheat roots are taking up Cd from the soil. Johnsson et al. (2002), for example, showed in a tracing experiment where soil was spiked with a Cd radio-isotope, 15 to 45 % of the Cd uptake in wheat plants originated from the subsoil. Hence subsurface soil factors could be important in influencing uptake. Further, other soil constituents such as Fe and Al oxides and clay mineralogy, which can affect Cd availability in soils, may be important. These were measured for selected sites in this study, but showed only limited variation between sites (data not shown). It is also possible however that site specific management had some effect on Cd uptake between sites.

The effect of N fertiliser application on grain Cd concentration, investigated for a single cultivar (Reliance) for 16 sites sampled in 2016 where the rates of N fertiliser application were provided by the grower, showed despite a wide range in the amount of N applied between sites (0 to 321 kg N

ha^{-1}), there was no significant relationship (P = 0.139) with grain Cd concentration. The relationship was not improved using multiple linear regression with the inclusion of other factors such as the amount of irrigation applied to the site or grain yield. This is in contrast to several studies that have shown that N fertiliser application can increase Cd uptake in wheat grain (Li et al., 2011; Wångstrand et al., 2007), likely through soil acidification, changes in ion exchange and plant physiological processes.

Another management factor that has previously been reported to affect Cd uptake in wheat is irrigation (Gray et al., 2002; Quinn et al., 2011). There was no difference in grain Cd concentrations in the spring planted Reliance cultivar between irrigated and non-irrigated sites, but a significant (P < 0.001) irrigation effect for the autumn planted wheat cultivars, with higher grain Cd concentrations in the dryland wheat (0.129 mg kg^{-1} FW) compared to irrigated wheat (0.067 mg kg^{-1} FW) (Table 7.4). This is opposite to what was reported by Gray et al. (2002) and also Andersson and Bingefors (1985) who previously showed Cd concentration in the grain of winter wheat was positively correlated with the amount of precipitation in the growing season. Specifically, there was significantly lower Cd concentrations in drier years. Associated with the lower grain Cd concentrations on the irrigated plots in the present study were significantly higher (P < 0.001) total soil Zn. Zinc is recognised as being able to compete with Cd for binding sites in soil and root surfaces and also compete with Cd for transport across the root cell membrane (Hart et al., 2002). Furthermore, studies have in some instances reported the application of Zn to soils can reduce Cd concentrations in wheat grain (Oliver et al., 1994). It may be that the higher soil zinc concentrations at the irrigated sites are important in reducing Cd uptake, although this would require further investigation where other confounding factors such as irrigation are removed.

There were also no differences in grain Cd concentrations between irrigated and non-irrigated sites in autumn planted Empress cultivar (Table 7.4), apart from one autumn planted site which had significantly (P < 0.05) higher grain Cd concentrations under irrigation (0.085 mg kg^{-1} FW) than the non-irrigated site (0.059 mg kg^{-1} FW). This was the only site where wheat from an irrigated and non-irrigated site were located in paddocks adjacent to each other and hence the potentially confounding influence of different soil factors was eliminated. Wheat yields on the irrigated site (12.4 t ha^{-1}) were also twice that of the dryland wheat (6.7 t ha^{-1}). An earlier New Zealand study also found that wheat under irrigation had both higher wheat grain yields and Cd uptake than dryland wheat crops (Gray et al., 2002). It was suggested this was simply the result of increased root interception and enhanced mass transport of Cd driven by higher transpiration rates of the higher yielding irrigated crop.

7.3.4 Managing Cd uptake in wheat

Grain Cd concentrations at some sites exceed or are approaching food standards in soils with Cd concentrations half the current Tier 1 trigger value in the TFMS of 0.6 mg kg^{-1} (Figure 7.2), and at total soil Cd concentrations considered as background (i.e. 0.13 mg kg^{-1}) (Cavanagh, 2014). Given that neither soil properties nor site management were useful predictors of grain Cd concentrations, this indicates that other options should be considered to manage Cd uptake. The significant variation found in Cd uptake between wheat cultivars highlights the potential to use low Cd accumulating cultivars at sites where there is high Cd uptake to reduce the risk of Cd accumulation approaching MLs. To advance the idea of managing the Cd risk through cultivar genetics would require the addition of Cd uptake as a standard assessment trait in plant breeding programmes. This is not currently in place in New Zealand, but has been implemented overseas (Grant et al., 2008).

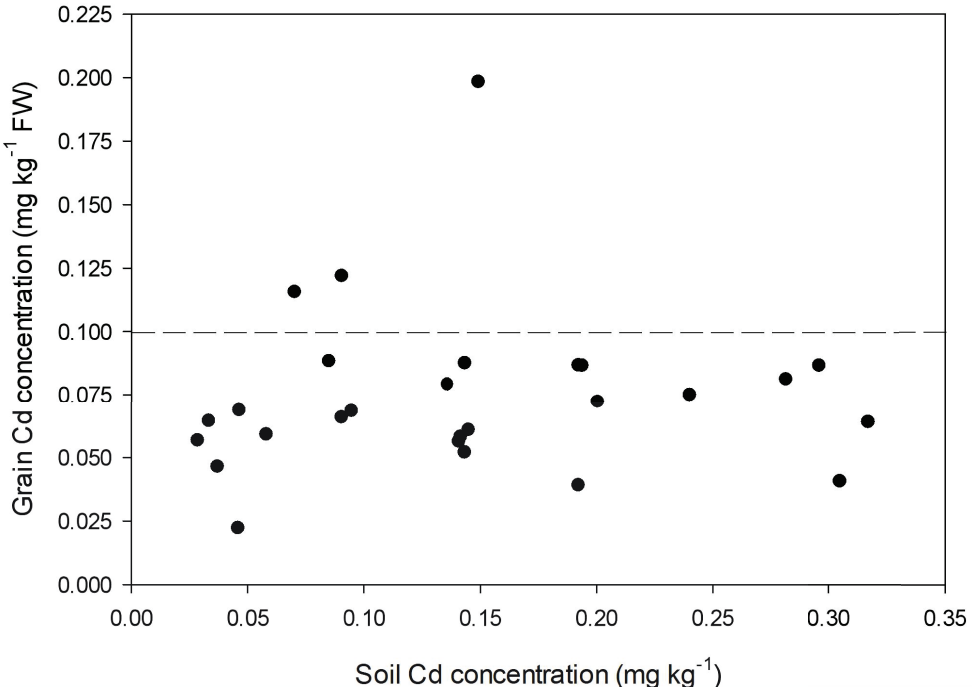

Figure 7.2 Relationship between total soil Cd concentrations (mg kg^{-1}) and mean grain Cd concentrations (mg kg^{-1} FW) for the Reliance cultivar. The dashed line is FSANZ maximum limit of 0.1 mg kg^{-1} FW.

Another consideration is the relevance of the food standard. Food standards are set according to the principle of being as low as reasonably practicable while still ensuring the protection of human health. Flour is the main product that is consumed, and we showed it typically has lower Cd

concentrations than the whole grain and the bran. It may be relevant to consider separate food standards for flour, and bran as a second tier of testing. We also note that the European Union standard for Cd in wheat is 0.2 mg kg^{-1} FW. It may be relevant to review the current FSANZ food standard as to whether the principle of the food standard is being met.

7.4 Conclusions

Cadmium concentrations in wheat grain varied between sites, with the average Cd concentrations below national and international food standards. Nonetheless, at seven sites, Cd concentrations exceeded, and at a larger number of sites, approached the ML. Surprisingly Cd in grain was reaching MLs at soil Cd concentrations that would be considered low by New Zealand standards. There was approximately a 2.5-fold range in grain Cd concentrations grain between cultivars. Given the lack of any strong relationships between soil properties and Cd uptake in grain or management factors and Cd uptake, the use of low-Cd-accumulating cultivars appears to offer the only effective way to mitigate Cd uptake in wheat grain at sites where Cd exceeds MLs. Incorporation of Cd uptake as a plant trait for routine assessment in wheat plant-breeding trials would offer this as an option for growers into the future. Further research should elucidate the extent to which wheat management practices such as irrigation or fertiliser type and application rates affect Cd uptake. Given that Cd uptake was in some instances high at sites with low soil Cd concentrations, research is also required to further explore the mechanisms of Cd uptake in wheat to support effective management of Cd.

Chapter 8

Effect of cultivar type and soil properties on cadmium concentrations in potatoes

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My contribution to this article: I completed the most of laboratories work on soil and plant samples analysis. I collated the data for field survey samples and joined the discussion for the writing of this manuscript.

8.1 Introduction

Cadmium (Cd) is a potentially toxic heavy metal and impurity in many phosphorus (P) fertilisers (Williams & David, 1973). As a result of extensive P fertiliser use, Cd has accumulated in some agricultural soils worldwide (Gray et al., 1999b; Jones et al., 1987; McGrath, 1986). There is concern regarding the accumulation of Cd in soils because it can readily be taken up by food crops (Baldantoni et al., 2016; Chaney & Hornick, 1978; Schroeder & Balassa, 1963; Zhao et al., 2015), and then has the potential to enter the human food chain through the crops and crop based products we consume in our diet (Clemens et al., 2013; Rietra et al., 2017).

Along with rice (*Oryza saliva* L.) and wheat (*Triticum aestivum* L.), potatoes (*Solanum tuberosum* L.) are an important staple food in many parts of the world, but also a source of Cd in the human diet (Fan et al., 2009; Rietra et al., 2017). Food standards provide for a safe level of intake over a lifetime. Therefore, while an occasional exceedance presents a low health risk, it could present a trade or reputational risk that ultimately affects the viability of potato production systems in New Zealand. It is therefore important that Cd concentrations in potatoes are maintained below maximum acceptable standards set by regulatory bodies. In response, research has been undertaken to identify which soil and plant factors influence Cd concentrations in potatoes to help manage Cd uptake in this crop (Fan et al., 2009; Maier et al., 2002; McLaughlin et al., 1994). In a survey of Cd concentrations in potatoes across 359 sites across Australia, McLaughlin et al. (1997b) reported topsoil chloride concentration were best related to Cd concentrations in potatoes with soil pH, total

zinc (Zn) and cultivar types only having a small influence on Cd concentrations. In Sweden, Öborn et al. (1995) found that a combination of organic matter content and increasing soil pH were negatively correlated with Cd concentrations in potatoes across 69 commercial field sites. Al Mamun et al. (2017) also showed the importance of increased soil pH and organic matter on reduction of Cd concentrations in potatoes. In contrast, Tack (2014) reported no relationship between potato Cd concentrations and topsoil pH and organic matter across 21 sites in Belgium. As well as soil factors, significant differences in Cd concentrations between potato cultivars has sometimes been reported (Ashrafzadeh et al., 2017; Dunbar et al., 2003; McLaughlin et al., 1994; McLaughlin et al., 1997b). Öztürk et al. (2011) for instance showed Cd concentrations in potato tubers ranged between 0.08 to 0.32 mg kg^{-1} DW in 16 cultivars from Turkey.

In line with many Western countries and South America, potatoes are a staple food in New Zealand and an important contributory source of dietary Cd (Pearson et al., 2018). Furthermore, potatoes are also a key export crop, worth an estimated $113 M in 2017 (Plant and Food Research., 2017). Few studies have measured Cd concentrations in potatoes in New Zealand (e.g. Ashrafzadeh et al., 2017; Kim, 2005; Roberts et al., 1995), and there is little information on the effects of soil properties and cultivar differences on Cd concentrations in potatoes across the main commercial growing areas (Pukekohe, Manawatū, Hawkes Bay and Canterbury). This information is important to determine if Cd concentrations in potatoes are currently compliant with national maximum limits (ML) for Cd of 0.1 mg kg^{-1} FW outlined in the Food Standards of Australia and New Zealand (FSANZ) standard 1.4.1.

In addition, to address the concerns of Cd accumulation in New Zealand soils, a Cadmium Management Strategy (CMS) based on an assessment of the risk Cd poses to agricultural systems has been released (MAF, 2011). The objective of the strategy is to ensure that 'Cd in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years'. The strategy outlines a risk-based framework for managing Cd accumulation in agricultural soils that focuses on a Tiered Fertiliser Management System (TFMS). The TFMS contains five tiers and four trigger concentrations, whereby as soil Cd concentrations increase, increasingly stringent fertiliser management practices are imposed. The trigger values are however considered only interim (Warne, 2011), because there was little New Zealand-specific Cd data available at the time to inform their development. As a result, some overseas soil guideline values were used. It is uncertain however how robust these overseas trigger values are for protecting New Zealand agricultural systems. Total soil Cd concentrations tend to be lower than many other countries (Roberts et al., 1994). However, there have still been occasional exceedances of our food standards for Cd (Gray et

al., 2001; Kim, 2005). Therefore, for some regions of New Zealand, the trigger values currently in the TFMS may not be sufficiently consistent with the CMS's objectives outlined above.

The development of New Zealand-specific risk-based trigger values firstly requires New Zealand-specific Cd data in a range of geographic areas, including plant concentrations in important food crops such as potatoes, along with information on the soil and plant factors which control Cd concentrations. The objectives of this study were i) to determine Cd concentrations in 10 economically important potato cultivars, and ii) to determine Cd concentrations in two potato cultivars grown across the main commercial potato cropping regions of New Zealand to assess the relationships between soil factors and Cd concentrations in potatoes.

8.2 Materials and methods

8.2.1 Sites and sampling

Soil cores and potato samples were collected from a combination of research trials and commercial field sites. In 2015, Cd concentrations were determined in 10 potato cultivars at Lincoln, eight at Pukekohe and two at the Waikato site (Table 8.1). In 2016 and 2017, Cd concentrations were determined in two commonly used potato cultivars (Moonlight and Innovator) grown across 35 commercial and research sites (Table 8.1). The sites covered seven of the 15 soil orders in New Zealand.

Table 8.1 Summary of sites and details of soil and plant sampling

Year	Sites	Location	No. of cultivars	Sampling details
Potato cultivar study				
2015	2 research trial sites	Pukekohe Waikato	8 2	Potato cultivars were grown in 3 replicate plots (double-row, 1.8 x 1.5 m), arranged in a randomised design. Soil and plant sampling were undertaken at harvest. For each plot 5 soil cores (150 mm depth) were collected and combined to form a single composite sample and a single tuber was collected from 5 plants within each plot. In addition a composite soil sample (25 x 150 mm) was taken along a 100 m transect.
	1 research trial sites	Lincoln	10	Potato cultivars were grown in 4 replicate plots (single row, 3.5 x 0.76 m), arranged in a randomised design. Soil and plant sampling were undertaken at harvest. For each plot, 5 soil cores (150 mm depth) were collected and combined to form a single composite soil sample and a single medium sized tuber collected from 5 plants within each plot. In addition a composite soil sample (150 mm depth) was taken along a 100 m transect.
Potato survey				
2016 and 2017	35 research trial and commercial sites	Canterbury Pukekohe Waikato Manawatū	2	At each commercial site 3 plots were established randomly across the field. These plots were the width of the planting row, by a length of ~1.5m sufficient to encompass a minimum of 5 plants. Within each plot, 5 tubers and 5 soil cores (150 mm depth) were collected At research sites, potatoes were grown and sampled as described above for the 2015 research trials at Pukekohe and Waikato.

8.2.2 Analysis

Soil and plant analysis

Soils were oven-dried (35^{o}C) and sieved (<2 mm) before analysis. Soil pH was determined in a 1:2 soil: water solution by potentiometric analysis (Blakemore et al. 1987). Exchangeable potassium (K), calcium (Ca), magnesium (Mg) and sodium (Na) were measured in a 1 M ammonium acetate extracted at pH 7 (Blakemore et al. 1987) and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Cation exchange capacity (CEC) was calculated by summing concentrations of extractable cations and extractable acidity. Bioavailable P (Olsen P) was determined by bicarbonate extraction (Olsen et al. 1954). Total carbon (C) and nitrogen (N) were determined by combustion using an Elementar Vario-Max CN Elemental analyser. Soil chloride concentrations were measured in a filtered 1:5 soil:water extract by ion chromatography. Pseudo total concentrations of Cd, Zn, P, aluminium (Al) and iron (Fe) were determined by microwave digestion using nitric acid and hydrogen peroxide as reported by Simmler et al. (2013); these will be referred to forthwith as total concentrations for simplicity. The digests were analysed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for Cd and ICP-OES for Zn, P, Al and Fe. Particle size analysis was measured using the pipette method (Claydon 1989).

Potato tubers were washed, peeled, roughly chopped, weighed, dried at 60°C to constant weight, and weighed again to enable reporting of data as fresh weight (FW) and dry weight (DW). Dried tubers were ground before digestion using the nitric acid and hydrogen peroxide microwave digestion method described by Cindrić et al. (2015). The digests were analysed for Cd by ICP-MS. In a selection of samples, peel was separated from the potatoes and the peel and flesh analysed separately for Cd and titanium (an indicator of soil contamination) by ICP-MS.

Quality control/assurance

Soil and plant samples were digested in batches of up to 40. Each batch included at least one digestion blank. One out of every 20 samples were analysed in duplicate to confirm repeatability of the analysis. Cadmium concentrations in procedural blanks were less than the detection limit and duplicate analysis of samples were within 5% of each other. The accuracy of soil and plant analysis was assessed using several internal and external certified reference materials including for soil (NIST Montana 2711; Interlab internal WEPAL soil 921; Interlab internal WEPAL soil 981), and plant (NIST 1573a, tomato leaves; ASPAC internal clover; ASPAC internal beetroot). Analytical results were within 5% of the certified values. The method detection limit for soil Cd was 0.020 mg kg^{-1} and 0.005 mg kg^{-1} in plant material.

Statistics

Statistical analyses were conducted using tuber Cd concentrations expressed on a dry weight basis. Comparison of Cd concentrations in cultivars within a site and between sites was undertaken separately using one-way ANOVA and data checked for normality by assessing residual plots. The data was not required to be transformed and the effects were considered significant if they differed at the probability level of 5% based on Fisher's unprotected least significant difference (LSD) test. The relationship between the concentration of Cd in the tubers and soil characteristics was determined by linear and stepwise (forward) multiple regression analyses. All analyses were performed using GENSTAT for Windows v18.

Transfer coefficient

The transfer coefficient (TC) is a very commonly used measure to assess the transfer of inorganic contaminants such as Cd from soil to different plant organs (Alloway, 1990). In this study it was the Cd concentration in the potato tuber divided by the total soil Cd concentration equation (1):

$$TC = Cdtuber\ (mg\ kg^{-1}\ DW) / Cdsoil\ (mg\ kg^{-1}\ DW) \quad (1)$$

Equation (1) can be rearranged to indicate the soil concentration at which a specific plant concentration is reached at a given site, assuming conditions such as soil properties (and therefore TC) do not change. Using the food standard as the target plant concentration (Cdtuber limit), a conservative estimate of the soil concentration at which the food standard can be reached (nCdfood standard) can be calculated (Equation 2). As the food standard is expressed as fresh weight, this requires conversion to a Cd concentration based on dry weight. The mean and standard error of the dry weight of potato samples measured in this study was 19.9% (0.3). This is consistent with the dry weight value (20%) which has been used to transform fresh weight to dry weight in potatoes in several other studies (Ashrafzadeh et al., 2017; Fan et al., 2009; Oporto et al., 2007; Tack, 2014). A dry weight of 20% was therefore used in equation 2.

$$nCdfood\ standard\ (mg\ kg^{-1}) = Cdplant\ limit\ (mg\ kg^{-1}\ DW) / TC \quad (2)$$

These values are not intended as threshold limits, but rather provide an insight into soil properties influencing plant uptake and the Cd concentrations at which management to mitigate the risk of exceeding food standards may be considered.

8.3 Results and discussion

8.3.1 Effect of cultivar type - 2015

Cadmium concentrations in potato tuber cultivars ranged between 0.040 and 0.275 mg kg^{-1} DW (n=70) (Table 8.2), with a mean concentration of 0.135 mg kg^{-1} DW (0.032 mg kg^{-1} FW). The mean concentration is similar to that previously reported (0.140 mg kg^{-1} DW) in a survey of potatoes sold commercially in the Waikato region (largely grown in Pukekohe) (Kim, 2005), but higher than an earlier study (0.100 mg kg^{-1} DW) of potatoes grown at Pukekohe (Roberts et al., 1995). Although, if only considering potatoes from the Pukekohe site, the mean concentration in the present study (0.070 mg kg^{-1} DW) is lower than both previous studies. Cadmium concentrations are within the range of mean values reported in several overseas studies (0.02 – 0.40 mg kg^{-1} DW) (Fan et al., 2009; Karavoltsos et al., 2002; Lin et al., 2015; Luis et al., 2014; Norton et al., 2015; Öborn et al., 1995; Radwan & Salama, 2006; Thomas et al., 1972; Wolnik et al., 1983; Zurera et al., 1987). As reported the moisture content in our potatoes was 80% (w/w). Therefore, the FW Cd concentrations of the tubers ranged from 0.009 to 0.069 mg kg^{-1}. These Cd concentrations are lower than the FSANZ standard 1.4.1 ML for Cd in potatoes of 0.1 mg kg^{-1} FW, which is the same as the Codex Standard 193-1995 (Codex Alimentarius Commission (CAC), 2009) and European Commission food standards (EC 1661/2006) for peeled potatoes.

In some instances, potatoes are consumed without removing the peel. It is therefore important to also know what the Cd concentration is in the potato peel, and the relative mass of the peel to the whole potato. In a subset of samples, the potato peel and the flesh were separated and analysed for Cd. Results showed that in all instances, Cd concentrations in the potato peel were higher (1.3 - 2.3 fold) than the flesh (Figure 7.1). This is consistent with what others have previously reported for Cd (Corguinha et al., 2012; Norton et al., 2015; Šrek et al., 2012) and other trace metals such as Zn, Fe, manganese, nickel and copper (Šrek et al., 2012; Subramanian et al., 2011).

Although the peel contained higher Cd concentrations (0.041 – 0.080 mg kg^{-1} FW) than the flesh, it was determined for a range of cultivars (and different sized potatoes), the peel constitutes only 10 to 17% of the mass of the whole potato (data not shown). As a result, even if potatoes were prepared and eaten without removing the peel, Cd concentrations in the whole potato would still remain compliant with the ML of 0.1 mg kg^{-1} FW.

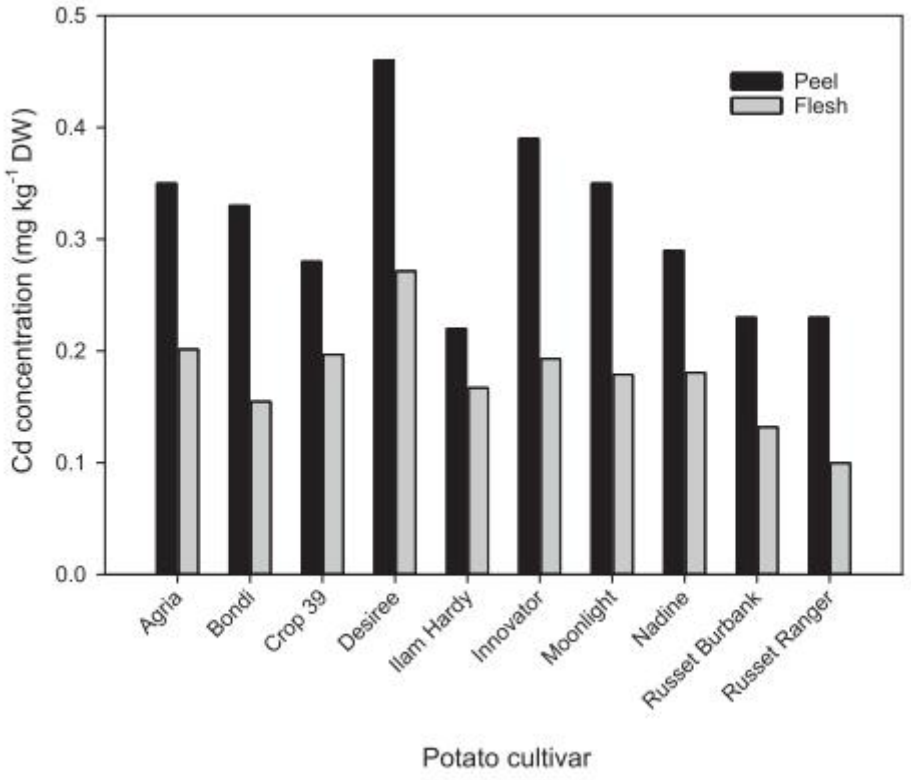

Figure 8.1 Comparison of cadmium concentrations (mg kg^{-1} DW) in the flesh or peel in potato cultivars from the Lincoln research trial site.

There were significant differences in tuber Cd concentrations between cultivars (Table 8.2). At Pukekohe and Lincoln, Cd concentrations varied 2.8 and 2.4 fold respectively, although the difference was less between the two cultivars grown at the Waikato site. Several studies have previously reported variation in Cd concentrations between potato cultivars (Corguinha et al., 2012; Larsson & Asp, 2011; Luis et al., 2014; McLaughlin et al., 1997b; Roberts et al., 1995). In some of these studies, Cd concentrations between cultivars varied by a similar magnitude as found in this study (Dunbar et al., 2003; Mengist et al., 2017), although others have reported a larger range. For instance, Ashrafzadeh et al. (2017) showed Cd concentrations in potato tubers ranged between 0.05 to 0.21 mg kg^{-1} DW in 10 cultivars grown at a single site in Lincoln, New Zealand.

Table 8.2 Potato tuber Cd concentrations (mg kg^{-1} DW) in different cultivars at Pukekohe, Waikato and Lincoln. Mean and standard error followed by the same lowercase letter within a site are not significantly different ($P < 0.05$) or not significantly different between sites (capital letters).

Cultivar	Pukekohe	Waikato	Lincoln
Agria	0.063abA	0.133aB	0.195abC
Bondi	0.073ab		0.150c
Crop 39	0.053bc		0.200ab
Desiree	0.063ab		0.275d
Ilam Hardy			0.158c
Innovator			0.205a
Moonlight	0.080aA	0.103bB	0.185bC
Nadine	0.113d		0.160c
Russet Burbank	0.070ab		0.123e
Russet Ranger	0.040c		0.115e

It is also important to note that while there were differences in Cd concentrations between cultivars, they were often inconsistent. At the Lincoln site for example, Desiree had the highest Cd concentration, but had one of the lowest Cd concentrations at the Pukekohe site. Nadine had the highest Cd concentration at Pukekohe but had one of the lower Cd concentrations at Lincoln. An exception was Russet Ranger, which had the lowest Cd concentration at both Lincoln and Pukekohe. It is not clear at present why there was this inconsistency. A next step would be to collect data on Cd concentrations in these cultivars across a greater number of sites and seasons to determine if this inconsistency is still maintained.

Compared to other crops (i.e. wheat, rice), there have been few studies that have investigated the mechanisms that control the variation in Cd concentrations in different potato cultivars. (Dunbar et al., 2003) and Mengist et al. (2018; 2017) both suggest differences are due in part to differential partitioning of Cd between organs (tuber, roots, stem and leaves) within the plant. Mengist et al. (2017) for instance found differences in both the shoot Cd concentration and leaf Cd mobilisation between a low and a high Cd accumulating cultivar. The high Cd accumulator had a higher shoot Cd concentration and remobilisation of Cd from leaves to tubers, thought to be driven by differences in shoot biomass (Mengist et al., 2018). Although, unlike Dunbar et al. (2003), Mengist et al. (2017) also indicate that differences in total plant uptake of Cd are important, with higher uptake in the high Cd accumulating cultivar, although the mechanism was not known. Regardless of the mechanism, the variation in Cd uptake in potatoes highlights the potential to use low Cd accumulating cultivars (e.g. Russet Ranger) at sites where there is high Cd uptake. Additionally,

including Cd accumulation as one of the traits in future cultivar evaluation trials, which at present is not common practice (Clemens et al., 2013), alongside more commonly assessed traits such crop yield and disease resistance should be considered.

A comparison of tuber Cd concentrations in two cultivars (Agria and Moonlight) grown at all three sites showed that Cd concentrations were highest at Lincoln, then Waikato and lowest at the Pukekohe site (Table 8.2). Cadmium concentrations were not related to the total soil Cd concentration, as the Lincoln site had the lowest soil Cd concentration (0.18 mg kg^{-1}), although it did have the lowest pH (6.0), a soil factor known to effect Cd availability in soils (Alloway, 1990). The comparatively low Cd concentrations in potatoes at Pukekohe may be a result of the high clay content (59%) and pH (6.5), both properties shown to limit Cd availability in soils (Chaney & Hornick, 1978; Tiller et al., 1997). The small number of sites and narrow range of soil properties in the 2015 trials limits any comparison between Cd concentrations and soil properties. As a result a larger comparison between Cd concentrations and soil properties was undertaken and reported below.

8.3.2 Survey of Cd concentrations in potatoes and soil properties – 2016 and 2017

Soil properties

Total soil Cd concentrations ranged between 0.09 – 0.86 mg kg^{-1} (Figure 7.2a). The mean concentration of 0.36 mg kg^{-1} is slightly higher than the mean Cd concentration of 0.28 mg kg^{-1} reported for cropping soils in New Zealand (Cavanagh, 2014). Most samples (88%) had soil Cd concentrations below the TFMS tier 1 trigger of 0.6 mg kg^{-1}. There were significant differences in total Cd concentrations between regions, with Waikato and Pukekohe higher than Canterbury and Manawatū-Whanganui (Figure 7.2a), in line with what is observed in larger surveys (Cavanagh, 2014). Other soil properties recognised as affecting plant concentrations of Cd also varied and are reported in Table 8.3. Soil pH ranged from low to high, while total C and CEC were low to medium (Blakemore et al., 1987). The majority of soils were classified as silt loams.

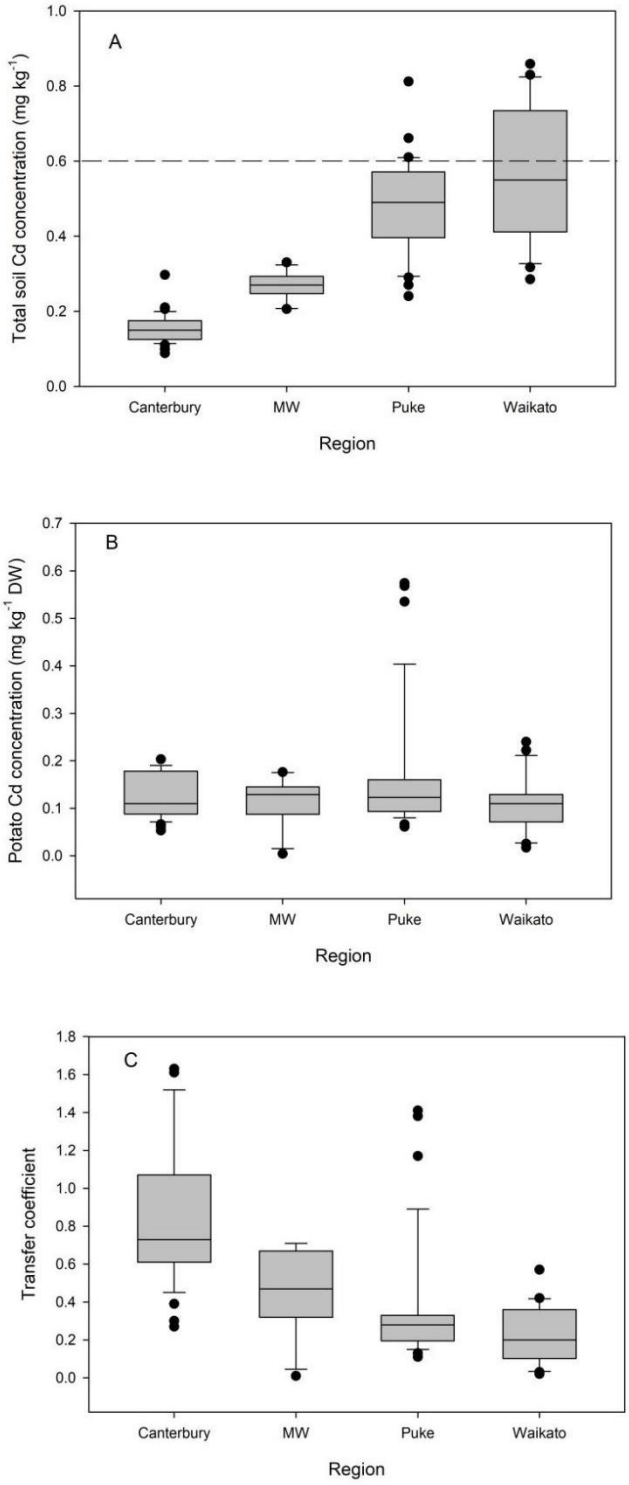

Figure 8.2 (A) Total soil cadmium concentration (mg kg^{-1}) in each region (MW = Manawatū–Wanganui; Puke = Pukekohe). The dashed line is the TFMS trigger 1 value. (B) Mean cadmium concentrations (mg kg^{-1} DW) in potatoes for each region. (C) The transfer coefficient for each region. Boxes depict the 25th and 75th percentile values, with horizontal lines plotted within boxes representing the median value. Whiskers show the 10th and 90th percentile values and the points the 5th and 95th percentile values.

Table 8.3 New Zealand soil order (Hewitt 2010) and mean concentrations of soil properties from the survey sites (0 – 15 cm)

Site	Soil Order	pH	Olsen P	Total P	Total C	Total N	Extractable				CEC	Total Cd	Total Zn	Cl	Sand	Silt	Clay
							K	Mg	Ca	Na							
			mg kg^{-1}	mg kg^{-1}	(%)	(%)	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	%	%
1	Pallic	6.0	28	n.d.	2.5	n.d	0.2	9.3	0.7	0.19	16	0.18	55	51	23	54	23
2	Pallic	6.0	25	835	1.9	0.2	0.1	6.9	0.5	0.14	13	0.12	72	13	7	70	23
3	Pallic	5.3	20	604	2.0	0.2	0.2	6.0	0.3	0.16	12	0.14	48	39	35	47	18
4	Gley	5.0	44	1031	3.5	0.3	0.5	6.8	0.5	0.20	17	0.19	79	24	11	69	20
5	Brown	5.4	36	740	1.6	0.2	0.6	6.5	0.9	0.09	17	0.14	71	12	15	62	23
6	Pallic	5.7	47	1030	3.3	0.3	0.5	8.2	0.8	0.24	15	0.16	82	38	7	67	26
7	Brown	5.4	30	947	2.5	0.3	0.4	6.6	0.7	0.12	14	0.14	79	38	13	62	25
8	Pallic	5.6	25	819	2.1	0.2	0.4	6.4	0.5	0.13	12	0.13	84	30	10	68	22
9	Pallic	5.5	29	1074	2.5	0.3	0.8	6.0	0.7	0.09	13	0.16	86	33	13	73	14
10	Pallic	5.5	50	774	1.3	0.1	0.5	4.2	0.5	0.10	9	0.11	72	58	28	55	17
11	Recent	6.1	48	892	2.4	0.2	0.4	6.6	1.3	0.19	13	0.15	90	29	13	66	21
12	Pallic	5.2	51	1156	2.5	0.3	0.7	9.3	1.5	0.19	18	0.24	96	57	6	67	27
13	Gley	5.0	78	1852	7.7	0.6	0.9	16.9	2.2	0.24	36	0.25	100	160	1	35	64
14	Organic	5.6	84	2141	7.8	0.6	0.5	23.9	1.6	0.22	38	0.21	88	70	1	43	56
15	Gley	5.2	55	1954	8.7	0.6	0.6	18.8	2.1	0.19	38	0.29	95	37	1	34	65
16	Gley	7.2	144	3418	2.4	0.2	0.9	12.9	0.7	0.08	15	0.30	103	4	12	61	27
17	Gley	5.4	92	2296	7.3	0.6	1.8	14.2	2.7	0.15	34	0.27	105	18	1	28	71
18	Granular	6.6	76	n.d.	1.6	n.d.	0.9	10.4	1.1	0.20	16	0.27	51	<10	21	20	59
19	Granular	6.9	303	3971	1.5	0.1	1.1	13.8	1.6	0.12	19	0.69	136	13	4	21	75
20	Granular	6.8	255	3161	2.3	0.2	1.3	13.9	1.5	0.11	19	0.54	139	49	4	24	72
21	Allophanic	6.0	136	2033	2.7	0.2	0.8	8.1	0.8	0.11	17	0.56	82	21	10	29	61
22	Granular	6.4	76	1732	3.7	0.3	0.7	11.9	0.8	0.11	19	0.40	82	17	8	34	58
23	Granular	6.8	146	2259	3.0	0.3	1.6	15.9	1.2	0.15	22	0.46	128	18	8	29	63
24	Granular	5.9	190	2839	2.2	0.2	0.8	9.2	1.1	0.21	19	0.54	122	28	7	30	63
25	Granular	6.4	171	4878	4.4	0.4	1.7	14.5	1.9	0.16	27	0.54	134	19	12	48	40
26	Granular	6.1	150	2540	2.5	0.2	1.6	10.3	1.5	0.07	20	0.52	125	12	7	30	63
27	Organic	5.9	74	1944	7.1	0.6	1.1	19.4	1.5	0.26	30	0.33	77	43	44	42	14
28	Granular	5.8	24	1073	6.0	0.5	0.5	13.0	0.9	0.22	25	0.43	71	34	8	31	61
29	Allophanic	6.6	54	n.d.	6.3	n.d.	0.8	13.5	1.4	0.10	22	0.77	76	<10	40	41	19
30	Allophanic	6.7	53	2590	4.0	0.4	0.8	13.1	1.2	0.07	20	0.74	98	42	31	47	22
31	Allophanic	6.0	65	1947	2.8	0.3	0.7	9.4	1.0	0.12	17	0.41	144	46	28	39	33
32	Allophanic	6.7	31	1611	3.6	0.4	0.8	10.9	1.3	0.07	18	0.32	68	n.d.	27	50	23
33	Allophanic	6.2	41	1953	4.2	0.4	1.0	7.1	1.2	0.05	17	0.50	83	3	28	51	21
34	Allophanic	6.9	73	2445	3.6	0.4	1.2	11.8	1.4	0.05	18	0.77	98	6	30	50	20
35	Allophanic	5.9	70	1981	3.6	0.4	1.0	7.5	1.0	0.08	19	0.53	125	9	27	47	26

n.d. not determined

Cadmium concentration in potatoes

Potato tuber Cd concentrations ranged between 0.004 and 0.574 mg kg^{-1} DW, with a mean concentration of 0.129 mg kg^{-1} DW (0.026 mg kg^{-1} FW) (Figure 7.2b), although 92% of samples had Cd concentrations < 0.20 mg kg^{-1} DW. With the exception of two of the three replicates from a single site at Pukekohe, Cd concentrations in potato tubers were well below the FSANZ limit of 0.5 mg kg^{-1} DW (assuming a dry weight content of 20%). The reason for the higher values at one of the Pukekohe sites is unknown as there were no obvious soil differences. Unlike the other sites surveyed, potatoes were the first crop at this site after it had been a long-term pasture.

There was no significant difference (P = 0.080) in the mean Cd concentrations between Innovator (0.111 mg kg^{-1} DW) and Moonlight (0.134 mg kg^{-1} DW). Furthermore, there was no significant difference in tuber Cd concentrations between regions (Figure 7.2b). This is in contrast with soil Cd concentrations and resulted in a marked regional variation in the transfer coefficient (Figure 7.2c), highlighting that the differences in tuber concentrations could be expected to be attributed to other soil properties affecting Cd bioavailability or total plant uptake. Very few studies have reported TC values for potatoes to allow comparison with the present study. An exception is Ashrafzadeh et al. (2017) who reported TC values between 0.095 to nearly 6.0 for ten cultivars from the same site.

Relationship between potato Cd concentrations and soil properties

There were no significant relationships between potato tuber Cd concentrations and soil factors commonly shown to affect Cd concentrations, such as organic C, CEC, total Cd, total Zn, and soil Cl concentration (McLaughlin et al., 1996) (Table 8.4). The only significant variables were total soil Al, extractable Na and base saturation, that individually explained at most 8% of the variation in potato Cd concentration. The majority (86%) of the data used for exploring the relationships were from a single cultivar, discounting plant factors confounding the relationships. As reported, comparison of Cd concentrations between the two cultivars were not significantly different. Hence, in the relationship analysis, cultivar difference would be small as one cultivar dominated the data and Cd concentrations did not differ between the two cultivars. Stepwise forward multiple regression analysis indicated a subset of six soil properties i.e. Al + Mn + Na + Fe + P + Zn accounted for 56.9% of the variation in potato tuber Cd concentration (Table 8.5).

Table 8.4 Single relationships of Cd concentration in potatoes (DW) with soil properties

Soil property	Significance level (p-value) of the relationship
pH	0.065
Olsen P	0.189
Exchangeable K	0.058
Exchangeable Ca	0.573
Exchangeable Mg	0.371
Exchangeable Na	***0.002 S***
CEC	0.156
Base saturation	***0.023 S***
Total Cd	0.709
Total Zn	0.578
Total P	0.052
Total N	0.056
Total C	0.070
C/N	0.122
Total Fe	0.477
Total Mn	0.529
Total S	0.621
Total Al	***0.010 S***

Note: ***S*** indicates a statistically significant relationship at 5% level. Significant relationship were positive except for base saturation.

Table 8.5 Coefficients of soil properties and their significance levels

Soil property	Coefficient	SE	% variation
Al	0.1275	0.0139	41.5***
Mn	- 0.0535	0.0113	*0.3****
Na	0.0199	0.0069	*9.5***
Fe	- 0.0479	0.0105	*0.7****
P	- 0.0677	0.0103	*4.8****
Zn	0.0304	0.0112	*0.1***

, * Significant at P <0.01 and 0.001 levels, respectively

It is uncertain why there were no significant relationships between soil properties such as pH and total Cd which have been previously shown to be important for Cd uptake in potatoes, although the absence of relationships is not unique to this study (e.g. Norton et al., 2015). It may simply be that compared to studies that have reported relationships (McLaughlin et al., 1997b), soil properties in the current study are a lot narrower in range. The lack of a relationship between tuber Cd

concentration and CEC may in part be related to the method used to measure CEC. Cation exchange capacity measured using neutral ammonium acetate opposed to the extracting the soil at its field pH, may have overestimated CEC, particularly in the variable charged soils in this study (i.e. Allophanic, Organic). It is also possible that site specific management (e.g. irrigation and fertiliser (quantity, type) application) that has been shown to influence Cd uptake in other crops such as wheat and flax (Grant et al., 1995; Jiao et al., 2004; Li et al., 2011) had some effect on Cd uptake between sites. Another factor that may have confounded results was differences in crop yield between sites. An increase in yield for example for any given cultivar may result in a decrease in that cultivar's Cd concentration. Although requested, yield data was not consistently provided by growers to allow testing of a crop yield effect.

8.3.3 Management of Cd concentrations in potatoes

To provide an approximation of the total soil Cd concentrations above which food standards might be exceeded, nCdfood standard values were derived at individual sites. The mean and 95th percentile range were 0.7 mg kg^{-1} (0.31 – 1.4) in Canterbury, 2 mg kg^{-1} (0.4 – 3.54) in Pukekohe, 2 mg kg^{-1} (0.7 – 7.04) in Manawatū -Whanganui and 4.7 mg kg^{-1} (1.19 – 16.7) in the Waikato. There was large variability in values, both within and between regions. This large variability has been noted in other studies. For example, de Vries and McLaughlin (2013) reported critical limits for potatoes in Australia between 0.147 – 0.959 mg kg^{-1}, reflecting the effect of soil pH and soil texture on Cd uptake. Despite the variability, and with the exception of Canterbury, potatoes grown in soils within the upper acceptable limit of the TFMS may be expected to remain within food standards.

In regions such as Canterbury where Cd uptake is high at relatively low soil Cd concentrations, and there is an absence of relationships with soil properties, cultivar management is potentially the best option for ensuring Cd concentrations in potatoes remain compliant with food standards if soil Cd concentrations continue to increase over time. Further, while there is no immediate urgency to identify low-Cd-accumulating cultivars as tuber concentrations are generally much lower than the FSANZ food standard, it would be prudent that potato breeding and selection trials should include Cd uptake as a plant trait to ensure that if high Cd accumulating cultivars are identified across a range of sites, that they do not become widely grown.

8.4 Conclusions

This study indicates there is variability in Cd concentrations in potatoes throughout New Zealand, and generally concentrations are much lower than the FSANZ ML. There were significant differences

in Cd concentrations between potato cultivars. There were no significant relationships between soil properties such as pH and total Cd which have been previously shown to be important for predicting Cd concentrations in potatoes. With the exception of Canterbury, the derived soil Cd concentrations at which ML for Cd in potatoes might be reached are greater than the upper acceptable limit of the TFMS. Management of Cd in potatoes is likely to be most effective through the use of low-Cd-accumulating cultivars or at least avoiding the wide-spread growing of high-Cd-accumulating cultivars if they are identified from further screening studies. Further studies to determine if other management factors such as irrigation or fertiliser type and rate on Cd concentrations in potatoes are needed.

Chapter 9

General discussion and conclusion

The aim of this project was to investigate the effect of environmental parameters and specific agricultural management practices on the accumulation of Cd in NZ agricultural soils and its uptake by plants. Research associated with soil Cd contamination conducted in NZ was reviewed in order to evaluate the present status of soil Cd concentration in NZ agricultural system and identify the environmental variables and farm management practices which influence soil Cd accumulation and its bioavailability. The following studies were performed to investigate the distribution of Cd concentration between soils and plants under field conditions. This is of particular concern because field assessments of the relationship between soils, plants species and cultivars and farm practices on Cd accumulation in plants can provide higher accuracy for the development of New Zealand specific risk-based Cd management guidelines. Additionally, Cd concentrations in NZ agricultural soils in the next 25 years have been modelled to assess the risk of the soil Cd concentration exceeding an assumed soil limit (1 mg kg^{-1}) and its possible implications for farmers in different farming systems and regions of New Zealand. The main findings of this research are summarized and discussed within this chapter.

9.1 Summary of results

9.1.1 Chapter 2

In chapter 2, a review of literature was conducted with an objective to summarise the studies on soil Cd in New Zealand and analyse the factors influencing Cd accumulation in soils. Historic applications of Cd-rich fertiliser is the major source of additional Cd in NZ agricultural soils. Intensively farmed lands, such as those used for dairy farming and arable cropping, have significantly higher soil Cd concentrations than those used for other farming practices. Apart from P application, the distribution of soil Cd concentration is strongly influenced by soil chemical properties. Soils with higher clay content, organic matter concentration and Fe, Al and Mn oxides tend to accumulate higher concentrations of Cd. This is supported by the soil monitoring data from the New Zealand Fertiliser Association indicating that Volcanic and Organic soils have the highest Cd concentrations. Cd accumulation in NZ soils is also linked to biotic effects (plant cultivar and species, and animal behaviour), climatic conditions, land slope, soil depth and the contact time between Cd and the soil.

In terms of the Cd mass balance, Cd inputs in NZ are mainly determined by the amount of P fertiliser application or Cd concentration in P fertiliser. Cd lost via leaching accounts for the highest proportion of Cd output. The reduction of Cd concentration in P fertiliser in recent decades has resulted in a decline of the national net Cd accumulation rate. Aa a result, it has been reported that at some sites Cd concentrations are no longer increasing, or in some cases, a decrease has been observed. However, soil Cd is likely to continue to accumulate in intensive farming systems or soil organic C-rich specific sites. The variability of distribution in soil Cd concentration between regions highlights the effects of P fertiliser usage and soil type on soil Cd accumulation.

9.1.2 Chapter 3

The objective of this chapter was to compare different measures of soil Cd (total Cd concentration in soil, Cd concentration in solution, $Ca(NO_3)_2$ extractable Cd concentration and DGT measured Cd concentration) and select the best one for predicting soil Cd availability. In this study, 147 paired soil and plant samples, with localized climate data, were selected randomly from a wider survey, which investigated the relationship between Cd concentrations in cropping soils and plant tissues (Chapter 6-8), to evaluate the response of plants to different measures of Cd. Of the four methods examined, single regression analysis results revealed that there was no single method accounting for the variation of Cd accumulation for all four plant species. Soil total Cd concentration accounted for 58.9% of the variation in Cd accumulation in spinach. $Ca(NO_3)_2$ extractable Cd had the highest predictive power (25.9%) for variability in onion Cd concentration, while no significant relationship was observed between different measures of soil Cd concentration and Cd concentration in potato. Various relationships between plant Cd concentration and measured bioavailable Cd concentration indicated that the applicability of soil extractants for the prediction of Cd uptake by plants was species dependent. Stepwise multiple linear regression models were also employed to explore the relationships between soil properties, climatic conditions, available Cd concentrations measured by four methods, and Cd uptake by four crops. The results showed that regional effect (site location) was an important explanatory variable in each regression model. Region effects and $Ca(NO_3)_2$ extractable Cd could explain 59.6% of variation in Cd concentration in onion. Olsen P concentration was an important explanatory variable in the variation of spinach Cd concentration. In terms of Cd concentrations in potato tuber and wheat grain, the regression models had more explanatory variables. Incorporating a climatic variable (air average temperature), $^{Cd}C_{DGT}$, soil total P concentration and region effects accounted for 76.7% of total variation in potato Cd. 66.8% of the variation in wheat grain Cd concentration could be explained by soil Olsen-P, soil solution Cd and

plant Zn concentration. The relationship between plant Cd and soil Cd concentrations measured by different methods was environmental and plant factor dependent.

9.1.3 Chapter 4

The research objective of Chapter 4 was to evaluate the effects of lime (and sulphur) and municipal compost and their interactions on Cd uptake by potato and wheat under field conditions. Liming significantly increased soil pH and compost significantly raised soil C concentration. Following the effects on soil pH, liming reduced $Ca(NO_3)_2$ extractable Cd concentration consistently in four trials. Compost also influenced $Ca(NO_3)_2$ extractable Cd concentration significantly in four trials. The reductions of Cd concentration in $Ca(NO_3)_2$ extractants in response to compost application were significant at low soil pHs, but not in high soil pHs. In contrast to the effects on soil Cd availability, the effects on Cd concentrations in plant edible parts varied between site locations. Potatoes grown in Canterbury had the highest Cd concentration in tubers in three potato field trials. In each trial, the effects of additional amendments on Cd concentration in potato were not significant. With regard to wheat, liming significantly increased Cd concentrations in wheat grain.

9.1.4 Chapter 5

The objective of this chapter was to provide a probabilistic risk-based assessment of future Cd accumulation in NZ agricultural soils. The data set from a national soil survey of measured Cd concentrations was used to model soil Cd accumulation in the next 25 years using the Monte Carlo framework. In this modelling exercise, the effects of soil type, farming practices, irrigation levels, P application rate and Cd concentration in fertiliser were taken into consideration. The model was validated by monitoring the soil Cd concentrations from the Winchmore Research Station. The estimated soil Cd concentrations from the SCM model between 1952 and 2003 coincided closely with the topsoil measured Cd concentrations.

The SCM models indicated that leaching is the most important process governing Cd output, while the effect of Cd removal via plants on Cd accumulation is negligible. The SCM simulations also suggested that fertiliser Cd concentration plays an important role in soil Cd enrichment. The SCM model revealed that organic soils had the largest potential to accumulate Cd, due to their high soil C content and low bulk density. On the contrary, sedimentary soils had the lowest Cd accumulation rate. Irrigation inducing Cd leaching poses negative effects on the increase of soil Cd concentration. Under the simulations conducted based on a 25 year timeline using current maintenance fertiliser recommendations (35 - 45 kg P ha^{-1} yr^{-1}) and the current long-term average Cd concentration in the

phosphate fertilisers (184 mg Cd kg^{-1} P), the soil Cd concentration in the Waikato will experience a slight increase while no obvious upward tendency of soil Cd is predicted in Canterbury. In the next 25 years, if P fertiliser application is at rate of 45 kg P ha^{-1} yr^{-1}, over 50% of dairy farms in Waikato are likely to reach 1.0 mg Cd kg^{-1} soil. At a national level for dairy systems this percentage is 22.6% if no irrigation is applied.

9.1.5 Chapter 6

Chapter 6 involved a field study, which represents common lettuce, spinach and onion cropping environments. The objectives of this chapter were to investigate the distribution of concentrations of Cd in onions, lettuce and spinach in New Zealand, and determining the influence of plant and soil variables on Cd uptake in these crops. The study involved soil sampling at 51 sites across the North Island and South Island. The main finding was that mean spinach Cd concentration was 0.06 mg kg^{-1} (fresh weight, FW), ranging from 0.005 to 0.11 mg kg^{-1}. The average bunching spinach Cd concentration (0.1 mg kg^{-1}) had reached the maximum guideline value for the NZ food standard (FSANZ ML, 0.1 mg kg^{-1}). The Cd concentrations in lettuce ranged between 0.005 and 0.034 mg kg^{-1} (FW), markedly lower than those in spinach and the FSANZ ML of 0.1 mg kg^{-1} (FW). The onion Cd concentration in this survey varied from 0.007 and 0.05 mg kg^{-1} (FW), which was also lower than the FSANZ ML of 0.1 mg kg^{-1} (FW). The results showed that cultivar variation contributed to the significant difference of Cd concentration in lettuce and onion. In terms of soil properties, the results of multiple regression analysis indicated that soil Cd concentration, pH and region significantly predicted Cd concentration in onions. Soil Cd concentration and carbon were explanatory variables accounting for the the variation in Cd concentration in bunching spinach. However, compared to the effects of crop cultivars on Cd accumulation in plants, soil-plant relationships explained only a low-moderate proportion of Cd in plants.

9.1.6 Chapter 7

The objectives of Chapter 7 were to assess the effects of plant factors (cultivars), soil properties and crop management practices on Cd uptake by wheat grain under field conditions. In 2015, Cd concentrations in 12 wheat cultivar samples, which were collected from three typical wheat growing sites in the South Island of NZ, were compared. The results showed that the Cd concentration in wheat grain varied significantly between cultivar varieties and growing sites. In 2016-2017, a larger number of wheat grain samples (plus paired soils) were sampled at the sites where two wheat cultivars were grown across the North and South Islands. Soil Cd concentrations at the wheat sites were generally low (average at 0.13 mg kg^{-1}), but the Cd concentration in wheat grain approached

FSANZ ML of 0.1 mg kg^{-1}, with 11 samples exceeding this current food standard. Single and Multiple regression analyses indicated a weak relationship between soil properties and Cd accumulation in wheat grain. The effect of N fertiliser application rate and irrigation (except at a single autumn wheat site) on Cd uptake by wheat grain were also insignificant. The significant variation of Cd concentration between wheat cultivars suggested the potential to develop low Cd enrichment cultivars to control the Cd risk on food security.

9.1.7 Chapter 8

In Chapter 8, the Cd concentration in potato tuber (another staple food crop) was compared between cultivars and sites with an objective to investigate the effects of plant and soil factors on Cd uptake by potato. 10 potato cultivars were grown in Canterbury, eight in Pukekohe and two in the Waikato in 2015 and were used to evaluate the effect of cultivar varieties on Cd uptake in potato. The main finding was that Cd concentrations in potato in Canterbury were generally higher than those in Waikato and Pukekohe, although soil Cd concentrations in Canterbury were much lower. There were significant differences in the potato tuber Cd concentration between potato cultivars. Similar to the wheat trials, in 2016-2017, two commonly grown potato cultivars (Moonlight and Innovator) were sampled accompanied with paired soils at a larger number of sites throughout New Zealand. The results showed that the Cd concentrations in potatoes were generally much lower than the FSANZ ML, however, there was large variability between sites. Potatoes grown in Canterbury have the highest potential to reach the FSANZ ML of 0.1 mg kg^{-1} (FW), regardless of the lowest soil Cd concentration in this region. The effects of soil factors on Cd enrichment in potato were not significant.

9.2 General discussion

Modelling results showed that organic soils have the greatest potential to accumulate Cd, which is consistent with the findings by Gray et al. (1998) showing that soil pH and OC were the decisive factors determining Cd sorption on NZ agricultural soils. In comparison to a predicted decline of soil Cd concentration in European cropping soils (Six & Smolders, 2014), the SCM model estimated an increase of soil Cd concentration in NZ cropping soils, which may be due to a higher P application rate and a higher Cd concentration in P fertiliser in NZ than in Europe. A modelled increase in Cd concentration in dairy systems agreed with the observed results in the Waikato (Stafford et al., 2018c). In contrast to some international studies (de Vries & McLaughlin, 2013; Sheppard et al., 2009; Six & Smolders, 2014) where biosolid was an important Cd input in Cd mass balances, the Cd input via biosolids addition was set to be zero in the SCM model. This should not contribute to a significant

influence on the accuracy in the estimation of soil Cd concentration, because biosolids are not generally applied in NZ agricultural systems. In some circumstances, the induced-increase of Cd concentrations by the biosolids application have also been reported in NZ, such as on dairy soils (Carrick et al., 2014), Mānuka *(Leptospermum scoparium)* soils (V.P. Reis et al., 2016) and reforested degraded soils (Gutierrez-Gines et al., 2017), but their effects on soil Cd concentration may still be considered negligible in a short term. For example, in a Cd leaching study (Carrick et al., 2014) comparing the effects of the application of superphosphate, cow urine and dairy shed effluent (biosolids) on soil Cd mass balance in a periodic-irrigation dairy system, the results showed that the application of biosolids increased soil Cd concentration at a rate of 0.209 g ha^{-1}, more than 50-fold lower than with superphosphate applications (11.1 g ha^{-1}). Sometimes, irrigation is also considered as an important Cd input (de Vries & McLaughlin, 2013). Zhao et al. (2015) estimated that irrigation application contributed to soil Cd accumulation at the rate of 1 - 400 g ha^{-1} $year^{-1}$ in the double-rice cropping systems in South China. In a Cd mass balance model (de Vries & McLaughlin, 2013), the estimated irrigation consisted of 0.4 - 0.6 g ha^{-1} $year^{-1}$ additional Cd in Australian dairy systems. Due to similar farming systems, the application of irrigation may also account for a significant amount of Cd input in NZ, particularly in the Canterbury dairy system where the irrigation rates varied from 3924 to 10,016 m^3 ha^{-1} $year^{-1}$ (Flemmer & Flemmer, 2007). However, this is different from the observed results in the real situations. Salmanzadeh et al. (2017b) assessed that irrigation caused an average annual loss at 1.0 g Cd ha^{-1} from the top 10 cm and 9.8 g Cd ha^{-1} from the top 40 cm of the soil profile compared to the unirrigated soils in the Canterbury dairy farm systems. Combining the effects of both leaching and overland outwash, irrigation application may result in soil Cd loss, rather than Cd accumulation in the Canterbury. This is likely due to the low Cd concentration of irrigated water (below detection limits) (Carrick et al., 2014).

The strong Cd sorption in high pH and organic C soils results in a relatively low Cd bioavailability in these soils (Gray et al., 1999). The findings that soils with higher Cd concentrations in NZ generally have a comparatively lower Cd phyto-availablility, have been supported in some laboratory studies (Gray & Mclaren, 2006; Gray et al., 1999d) which indicates a dominant role of soil pH and organic matter concentration in determining soil extractable Cd concentration. In our study, the effects of these soils variables on Cd uptake by plant were investigated with a larger number of samples under field conditions. The results highlight the significant effects of region and plant species on the Cd transfer from soil to plants. In the Canterbury region which is dominated by sedimentary soils with a low soil pH and OC content, a higher Cd loss via leaching and crop off-take from this region may result in a lower soil Cd concentration compared to the Waikato region dominated by volcanic soils.

Volcanic soils which has an abundance of allophane (a hydrous aluminium silicate clay mineraloid with amorphous/poorly crystalline structure), are also known to stabilize organic matter and bind Cd, and therefore, contributes to a relatively lower Cd bioavailability (González-Costa et al., 2017; von Lützow et al., 2008). High soil Cd bioavailability contributes to the finding that crops (wheat and potato) grown in Canterbury have a higher potential to exceed the food standard of 0.1 mg kg^{-1} (FW). The mean estimated soil Cd concentration above which food standards may be exceeded in Canterbury is 0.7 mg kg^{-1} for potato, nearly two-fold lower than Pukekohe (2.0 mg kg^{-1}) and Manawatu-Whangunui (2.0 mg kg^{-1}). and five-fold lower than Waikato (4.7 mg kg^{-1}). Also, wheat is mainly grown in Canterbury. For most wheat grain samples collected, the Cd concentration is approaching the current food standard, although the average value is still within the safe level. However, the Cd concentration in wheat grain and potato tuber was not significantly correlated with the main soil variables, such as soil pH, total C and total Cd concentration. This is consistent with the previous findings in wheat (Gray et al., 2001) and potato (McLaughlin et al., 1997) under field conditions. In line with these studies, plant cultivars, rather than soil variables play a more significant role in determining Cd uptake by wheat and potato. In comparison, soil properties can significantly represent a low to moderate proportion of the variation in spinach and onion Cd concentration. Similar results were also reported by Yang et al. (2016), who showed that soil pH, total C and total Cd concentration could explain 56% variation of Cd in leaf vegetables. This may be because the movement of Cd in 'fruiting' vegetables (potato and wheat) is more complicated than leafy vegetables due to the influence of the bio-membrane on Cd translocation within plants (McLaughlin et al., 2011). Similar to root uptake processes where Cd is passively taken up through ion channels, the transfer of Cd within wheat and potato is controlled by a membrane between xylem and phloem, while the movement of Cd in spinach follows the water transport system which is influenced by transpiration. The high enrichment of Cd in spinach leaf in our study is likely due to its high transpiration rate (Khan et al., 2010; Tani & Barrington, 2005). Similar high PUF of spinach was also reported some studies (Al Mamun et al., 2016; Khan et al., 2010; Mishra et al., 2009), or other leafy vegetables, such as lettuce (Gaw et al., 2008; Gray et al., 1999a; Luo et al., 2011) and radish leaf (Gaw et al., 2008). Of the four plant species in this study, 11 out of 22 soil variables exhibited a Spearman correlation coefficient with Cd concentration in spinach leaf that was at the 0.05 probability level of significance. The highest regression line gradients (R^2_{adj}) indicated the strongest relationship between spinach leaf Cd concentration and soil total Cd concentration. The variation of plant Cd concentration responding to soil variables may also be due to the soil depth at which plant roots take up Cd. Thorup-Kristensen (1999) found that a crops' rooting system was influenced by the duration of growth. Due to a short growing season, spinach may have a shallow root system when

harvested (Thorup-Kristensen, 1999), while the roots of potato and wheat mainly distribute in the 0 – 40 cm soil layer under the field conditions (Thorup-Kristensen, 1999; Wang et al., 2006b; Zhang et al., 2004). In terms of potato root systems, Wang et al. (2006b) found that the top 10 cm soil layer only contained 26 – 41% of root length density, although it had 63 - 82% of total root weight density. This means that there are a considerable amount of fine roots distributed in the deeper soil horizons. In a Cd radio-isotope tracing experiment, Johnsson et al. (2002) found that 15-45% of the Cd accumulated by wheat were from the subsoil horizons. In this study, soils were sampled from the top 15 cm, which might be shallower than the actual depth of root placement. This may also explain the discrepancy of soil $Ca(NO_3)_2$ extractable Cd and Cd concentration in potato responding to the addition of soil amendments in Chapter 4.

In Chapter 3, there is no single method accounting for variation of Cd accumulation for all four plant species. Consistent with previous studies, multivariate regression analysis also indicated that the predictive capability of pseudo-total Cd, 0.05 M $Ca(NO_3)_2$ extractable Cd, the DGT measured Cd and soil solution Cd concentration are environmental (Song et al., 2015) and plant factor (Almås et al., 2006) dependent. The factors likely influencing the predictive capability of measures of metal availability in Cd uptake by plants are mainly fertiliser status, climatic condition and plant Zn concentration. The results in field trial experiments in Chapter 4 showed that the application of lime and compost significantly impacted soil $Ca(NO_3)_2$ extractable Cd concentrations, confirming the dominant role of soil pH and soil OC in governing soil Cd solubility, which has been widely reported in previous studies (Al Mamun et al., 2016; Al Mamun et al., 2017). However, the reduction of Cd accumulation in wheat grain responding to liming may likely be confounded by the liming-induced Zn deficiency. Similar liming-induced increase in Cd concentration in carrot, potato and cereal grain was reported by Jansson, (2002). They concluded that liming could only reduce the Cd concentrations in crops which were grown in the soils with high levels of Cd concentration, while promoted Cd uptake by plants if soil Cd concentrations were low. In NZ, the increase of Cd concentration in respond to liming was reported in mustard (Bolan et al., 2003b) and ryegrass (Benyas et al., 2018). On the contrary, compost was more consistent in the reduction of the wheat Cd concentration. This may be due to a high Zn concentration in compost (used in this study) and the compost-born soft Lewis bases (e.g. -SH group). The soft Lewis bases can bond Cd^{2+} more strongly than Zn^{2+} (Alloway, 1990; Welikala et al., 2018). However, the reduction of Cd concentration in wheat grain induced by compost addition is pH dependent. The formation of soluble organo-metal complexes at high soil pHs may increase the bioavailability of soil Cd (Smolders & Mertens, 2013).

This may be the reason why there are no significant interaction between liming and compost addition on soil $Ca(NO_3)_2$ extractable Cd and plant concentrations in our study. However, the effect of amendment addition on Cd uptake by potatoes varied between sites, consistent with Chapter 3 highlighting the importance of the effect of region (site location) on Cd accumulation in plants. Potatoes grown in the Canterbury had significantly higher Cd concentrations where the lime and compost did not pose significant effects on Cd concentration in potato tubers. On the contrary, an unexpected liming-induced decline in potato Zn concentration occurred. This implies that the development of soil-based Cd risk management guidelines should be site-specific. In a pot experiment, Al Mamun et al. (2017) observed a significant reduction of both soil extractable Cd and potato tuber Cd concentration in response to lime and compost addition. Different from the field trials, pot experiments have more homogeneous distribution of soil variables and larger root density which may contribute to more thoroughly interaction between soils and roots and consequently accentuate the effects of additional amendments on plant Cd uptake. Consistent with the suggestions made by Friesl et al. (2006), our results also show that pot experiments cannot fully replace field trials to evaluate the effectiveness of soil Cd amendments. In our field trial experiment, artificially high rates of lime application raised soil pH to around 7.0 (7.2 in Pukekohe) with the aim to test effects of pH changes on Cd uptake by plants. From a practical perspective, the designed soil pHs in this study are higher than typical values in the real NZ cropping environment. This means that liming-induced micronutrient deficiency may not occur in the real process of cropping production. Cd may enter into soils with the application of compost, occurring as an impurity. In this study, no significant increase of soil Cd concentration induced by compost addition was observed. However, the application of compost can increase soil organic C concentration, which may increase the possibility of the soil Cd accumulation over long timeframes, as the SCM model indicates that organic soils have the largest potential to accumulate Cd.

9.3 Conclusions

This research showed that mean Cd concentrations in lettuce, wheat, onion and potato are much lower than the FSANZ ML of 0.1 mg kg^{-1} (FW), while Cd concentrations in baby spinach and bunching spinach at some sites are approaching or exceeding this current NZ food standard. There were significant differences in plant Cd concentrations between species: concentrations in leafy vegetables (spinach and lettuce) are generally higher than those in onion bulb, potato tuber and wheat grain, and there concentrations varied significantly between different cultivars. At a national scale, Cd concentrations in spinach and onion positively correlated to soil total Cd concentration. The effect of soil properties on Cd accumulation in wheat and potato are insignificant. Potato and

wheat grown in Canterbury have a large potential to accumulate Cd to higher concentrations than those grown in Waikato Manawatu-Wanganui, Hawkes' Bay and Pukekohe (Auckland).

There are four measures used to estimate Cd concentration in plants but there is no consensus that a single appropriate measure of Cd bioavailability successfully predicts Cd concentrations in four plants across eight regions. The predictive power of these methods in Cd bioavailability are environmental and plant factor dependent. The application of lime and compost can significantly reduce the soil bioavailable Cd concentration, however, their effects on Cd concentration in plant edible parts depend on the location of the growing site. There is also no significant interaction of lime and compost on soil Cd availability. The variation of Cd concentration in plants responding to the addition of amendments is inconsistent across sites. The development of guidelines of soil amendments application on Cd risk management should be site-specific.

The SCM model shows a balance occurring between Cd inputs and Cd loss in the Winchmore pastoral trials and suggests that leaching is the most important process governing Cd output. The accuracy in prediction of potential changes of soil Cd concentration can be influenced by a variety of factors, such as climate change, farm practices and their induced changes of soil properties. The SCM simulations indicate that Cd concentration in fertiliser is a decisive factor in NZ soil Cd accumulation. The estimation of soil Cd concentration is also influenced by soil order, P usage, irrigation and landuse. In the next 25 years if P fertiliser application is at a rate of 45 kg P ha^{-1}, the SCM model estimated 22.6% of NZ dairy farms are likely to reach 1.0 mg Cd kg^{-1} soil when no irrigation is applied. In the Waikato, this percentage is over 50% of dairy farms.

9.4 Suggestions for further research

Although the effects of soil and plant factors on the risk management of Cd in New Zealand agricultural soils have been investigated in this study, there are still many questions which need to be answered. The possible further studies could include the following areas:

1. The depth of soil sampling in field trial experiments or field surveys in this study were 15 cm, which may be shallower than the actual depth of plant root placement. Sampling soil in deeper soil horizons should be taken into consideration in further research.

2. Plant cultivar accounts for significant variations in plant Cd concentration, indicating that the development of low-Cd-enrichment cultivars may be an effective way to control the risk of Cd accumulation in plants.

3. The effects of soil amendments on the Cd concentration in potato tuber varied between the locations of the growing sites. The regression models in Chapter 3 also highlighted the importance of region in estimating Cd uptake by four plants. However, the site- (or region) specific effects on Cd accumulation in plants is still not understood in this study. Exploring the effects of site-specific mechanisms on Cd uptake by plants is required for future research.

4. In the SCM model, the coefficients of partitioning Cd between the solid phase and solution phase (K_d) were not fully calibrated against various NZ soil types, which may increase the uncertainty when generalizing this model for all NZ agricultural soils. Therefore, a comprehensive calibration of K_d in other main soil orders would increase the accuracy in the predication of the soil Cd concentration.

5. McDowell (2010) estimated that Cd loads in surface outwash caused a significant amount of Cd loss. However, the surface runoff Cd losses were not included in the SCM, due to insufficient available data. Further work is needed to explore the information on the volume of water loss via surface runoff and its Cd concentration.

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Appendix A

Supplementary information in Chapter 2

Table A1 Summary of research into plant Cd uptake in NZ

Plant		Type of study	Soil Cd (mg kg^{-1})		Plant Cd (mg kg^{-1}, DW)		Reference
			Mean	Range	Mean	Range	
Pasture	Grass	Field survey [a]	0.44	0.04 - 1.53	0.10	0.04 - 0.17	(Roberts et al., 1994)
		Field survey	0.34	0.25 - 0.49	0.26	0.17 - 0.35	(Roberts & Longhurst, 2002)
	Legume	Field survey [a]	0.44	0.04 - 1.53	0.06	0.03 - 0.07	(Roberts et al., 1994)
		Field survey	0.34	0.25 - 0.49	0.28	0.14 - 0.54	(Roberts & Longhurst, 2002)
	All pasture	Field survey	0.89	0.25 - 1.58	0.13	0.01- 1.55	(Reiser et al., 2014)
	Ryegrass	Greenhouse	0.36	0.03 - 1.34	0.17	0.07 - 0.30	(Gray et al., 1999a)
		Greenhouse	0.77	0.19 - 1.34	0.30	0.06 - 0.77	(Gray et al., 1999c)
		Greenhouse	3.20	---	0.61	0.38 - 0.85	(Gray & McLaren, 2005)
		Greenhouse	0.13	---	0.09	---	(Simmler et al., 2013)
		Greenhouse	0.08	---	0.05	0.03 - 0.09	(Gray & McDowell, 2016)
		Greenhouse	0.46	0.45 - 0.47	0.10	0.09 - 0.11	(Stafford et al., 2016)
		Field trial	0.46	0.13 - 0.79	0.09	0.04 - 0.14	(Cavanagh et al., 2016)
	White clover	Greenhouse	0.36	0.03 - 1.34	0.17	0.02 - 0.43	(Gray et al., 1999a)
		Greenhouse	0.77	0.19 - 1.34	0.31	0.08 - 0.97	(Gray et al., 1999c)
		Greenhouse	0.27	0.06 - 1.34	0.07	0.01 - 0.24	(Wakelin et al., 2016)
		Greenhouse	0.46	0.45 - 0.47	0.04	<0.01 - 0.06	(Stafford et al., 2016)
		Field trial	0.46	0.13 - 0.79	0.05	0.07 - 0.02	(Cavanagh et al., 2016)
	Plantain	Greenhouse	0.46	0.45 - 0.47	0.73	0.44 - 0.99	(Stafford et al., 2016)
		Greenhouse	0.70	0.61 - 0.79	0.47	0.21 - 0.65	(Stafford et al., 2018a)
	Chicory	Field trial	0.44	0.13 - 0.75	0.06	0.05 - 0.06	(Cavanagh et al., 2016)
		Greenhouse	0.46	0.45 - 0.47	1.64	1.48- 1.96	(Stafford et al., 2016)
		Field trial	0.46	0.13 - 0.79	0.38	0.35 - 0.41	(Cavanagh et al., 2016)
Crops	Wheat	Greenhouse	0.36	0.03 - 1.34	0.19	0.02 - 0.59	(Gray et al., 1999a)
		Greenhouse	0.77	0.19 - 1.34	0.13	0.06 - 0.26	(Gray et al., 1999c)
		Field trial	0.20	0.09 - 0.45	0.05	0.02 - 0.12	(Gray et al., 2001)
		Field trial	0.13	0.11 - 0.15	0.07	0.04 - 0.10	(Gray et al., 2002)
		Field trial	0.24	0.21 - 0.30	0.06	0.04 - 0.09	(Cavanagh et al., 2016)
	Lettuce	Greenhouse	0.36	0.03 - 1.34	1.76	0.27 - 4.50	(Gray et al., 1999a)
		Greenhouse	0.77	0.19 - 1.34	1.43	0.08 - 3.95	(Gray et al., 1999c)
		Greenhouse	0.23	0.03 - 0.54	1.24	0.30 -2.10	(Gaw et al., 2006)
		Greenhouse	0.99	0.47 - 1.50	0.79	0.58 - 0.99	(Al Mamun et al., 2016)
	Potato	Field trial	0.29	0.14 - 0.43	0.28	0.13 - 0.53	(Cavanagh et al., 2016)
		Field trial	0.41	0.17 - 0.80	0.21	0.07 - 0.41	(Cavanagh et al., 2016)
		Field trial	0.06	---	0.14	0.06 - 0.22	(Ashrafzadeh et al., 2017)
		Greenhouse	1.45	---	0.02	0.01 - 0.05	(Al Mamun et al., 2017)
	Carrot	Greenhouse	0.36	0.03 - 1.34	0.70	0.12 - 1.91	(Gray et al., 1999a)
		Greenhouse	0.77	0.19 - 1.34	0.52	0.14 - 1.27	(Gray et al., 1999c)
	Onion	Greenhouse	1.50		0.20		(Al Mamun et al., 2016)

Plant	Type of study	Soil Cd (mg kg^{-1})		Plant Cd (mg kg^{-1}, DW)		Reference
		Mean	Range	Mean	Range	
	Field trial	0.47		0.18		(Cavanagh et al., 2016)
Maize	Greenhouse	0.36	0.03 - 1.34	0.21	0.04 - 0.67	(Gray et al., 1999a)
Radish	Greenhouse	0.22	0.03 - 0.54	0.40	0.24 - 0.54	(Gaw et al., 2006)
Spinach	Greenhouse	0.99	0.47 - 1.50	0.86	0.52 - 1.21	(Al Mamun et al., 2016)

Table A2 P fertiliser product types and maximum rate of average annual P application in the Tiered Fertiliser Management System

Tier	Soil Cd (mg kg^{-1})	Average annual P application rate (kg P ha^{-1} $year^{-1}$)		
		Sulphuric acid derived products plus RPR	Phosphoric acid derived products	Nitric acid derived products
Tier 0	< 0.6	No restriction	No restriction	No restriction
Tier 1	0.6 - 1.0	45	60	105
Tier 2	1.0 - 1.4	40	55	105
	1.4 - 1.6	35	50	100
Tier 3	1.6 - 1.7	15	25	55
	1.7 -1.8	10	12.5	25
Tier 4	≥ 1.8	No net Cd accumulation	No net Cd accumulation	No net Cd accumulation

Data from Sneath (2015)

Appendix B

Supplementary information in Chapter 3

Table B1 The CRMs used for soils analysis

Reference Soils	Interlab internal: WEPAL soil 981			NIST: Montana 2711			Interlab internal: WEPAL soil 921		
	Cd	Zn	P	Cd	Zn	P	Cd	Zn	P
Size (n)	16	16	16	3	3	3	3	3	3
Reference value (mg kg^{-1})	0.34	46.10	1260	32 - 46	290-340	600-900	2.40	502.00	117
Detected value (mg kg^{-1})	0.33	42.46	1298	36.47	287.81	679	2.56	466.66	1262
Standard deviation	0.02	4.16	82.51	0.20	6.00	23.41	0.09	65.33	17.56
Variation	0.06	0.10	0.06	0.01	0.02	0.03	0.03	0.14	0.01
Recovery (%)	96.09	92.11	102.99	NA	NA	NA	106.69	92.96	107.81

NA: not available

Table B2 The CRMs used for plants analysis

Reference plants	ASPAC internal: Beetroot		NIST 1573A: Tomato leaf		ASPAC internal: Clover	
	Cd	Zn	Cd	Zn	Cd	Zn
Size (n)	14	14	11	11	3	3
Reference value (mg kg^{-1})	0.87	50.20	1.52	30.90	0.26	27.00
Detected value (mg kg^{-1})	0.83	51.87	1.41	31.92	0.24	28.58
Standard deviation	0.02	2.65	0.25	6.74	0.02	0.67
Variation	0.02	0.05	0.18	0.21	0.10	0.02
Recovery (%)	95.79	103.33	92.57	103.30	92.36	105.86

Table B3 Descriptive statistics of the elements content & physicochemical characteristics of sub-selected analysed soils and Pearson correlation coefficients (log transformation) for each soil parameter with soil total Cd and total Zn concentration.

Parameter	Minimum	Mean	Median	Maximum	Correl.Cd	Correl.Zn
pH	4.88	6.01	5.97	7.23	0.22**	0.01
Sand (%)	1	19	16	45	0.18*	- 0.16
Silt (%)	19	49	49	71	- 0.56**	- 0.18*
Clay (%)	14	32	27	76	0.23**	0.38**
Bulk density (g cm^{-1})	0.45	0.92	0.94	1.23	- 0.66**	- 0.26**
Olsen P (mg kg^{-1})	11	72	51	351	0.59**	0.45**
Total P (g kg^{-1})	0.53	1.84	1.60	5.08	0.87**	0.56**
Total C (%)	1.12	3.75	2.87	19.79	0.45**	0.07
Total N (%)	0.09	0.33	0.27	1.25	0.46**	0.10
K (mg kg^{-1})	728	3829	3570	11628	- 0.84**	- 0.17*
Ca (mg kg^{-1})	2020	6937	6544	45279	- 0.36**	- 0.20*
Mg (mg kg^{-1})	510	4703	4299	40435	- 0.75**	- 0.07
Na (mg kg^{-1})	161	376	300	1255	0.39**	0.07
CEC ($cmol_c kg^{-1}$)	10	21	19	48	0.52**	0.31**
Total Cd (mg kg^{-1})	0.02	0.37	0.29	1.35		0.33**
Total Zn (mg kg^{-1})	29.63	89.90	89.15	154.16	0.33**	
Extractable Cl (mg kg^{-1})	6.71	30.11	22.16	160.29	0.10	0.00
Soil Fe (mg kg^{-1})	5891	23730	21279	66971	- 0.22**	0.38**
Soil Al (mg kg^{-1})	16333	50997	36192	144385	0.54**	0.57**
Soil Mn (mg kg^{-1})	145	790	523	2829	0.52**	0.64**
Soil S (mg kg^{-1})	180	549	471	1971	0.70**	0.181*
$^{Cd}Ca(NO_3)_2$ (μg kg^{-1})	0.05	8.18	3.76	60.21	0.24**	0.23**
$^{Cd}C_{DGT}$ (μg L^{-1})	0.04	0.83	0.76	2.10	0.36**	- 0.05
^{Cd}Pore water (μg L^{-1})	0.06	18.37	21.01	76.32	0.29**	0.10
$^{Zn}Ca(NO_3)_2$ (μg kg^{-1})	0.10	283.67	99.40	2573.21	0.30**	0.19*
$^{Zn}C_{DGT}$ (μg L^{-1})	0.68	3.12	1.82	26.66	0.20*	0.08
^{Zn}Pore water (μg L^{-1})	44.26	282.65	253.86	781.70	0.08	- 0.07
Total rainfall (mm)	56	416	421	816	--	--
Temperature (°C)	8.94	14.51	14.41	21.85	--	--
Radiation (KMJ $M^{-2}\cdot d^{-1}$)	0.80	3.05	3.51	4.28	--	--

* $P < 0.05$, ** $P < 0.01$.

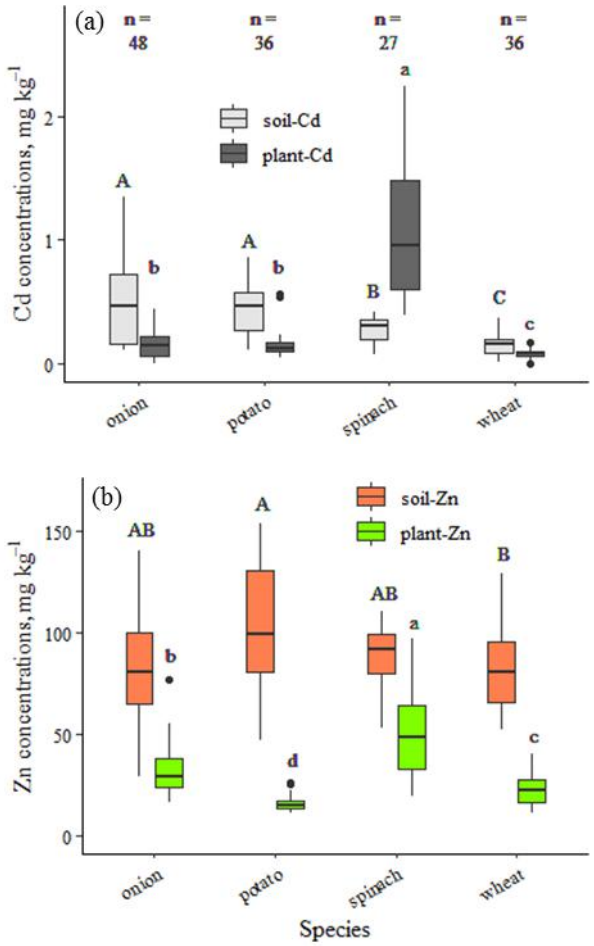

Figure B1 Boxplots of Cd (a) and Zn (b) concentrations in four cropping soils and plants showing median, 25th and 75th quartiles and the 5th and 95th percentiles as whiskers and the circles as outliers. Metal concentrations with the same letter mean that are not significantly different (P > 0.05) after Kruskall- Wallis test.

Appendix C

Supplementary information in Chapter 4

Table C1 The effects of applied amendments on soil total Cd and Zn concentrations in four experimental trials

Pukekohe potato trial Treatments		Soil Cd (mg kg^{-1})	Soil Zn (mg kg^{-1})	Manawatu potato trial Treatments		Soil Cd (mg kg^{-1})	Soil Zn (mg kg^{-1})
pH- 1	MC-0	0.49 ± 0.02 a	82.93 ± 4.07 a	pH- 1	MC-0	0.11 ± 0.01 a	49.18 ± 0.87 d
pH- 2	MC-0	0.47 ± 0.03 a	81.95 ± 7.10 a		MC-25	0.12 ± 0.02 a	50.54 ± 2.49 bcd
	MC-25	0.46 ± 0.03 a	82.48 ± 5.58 a		MC-50	0.13 ± 0.03 a	56.64 ± 5.18 a
	MC-50	0.41 ± 0.06 a	81.08 ± 4.65 a	pH- 2	MC-0	0.14 ± 0.02 a	52.38 ± 1.91 abcd
pH- 3	MC-0	0.45 ± 0.05 a	77.73 ± 4.50 a		MC-25	0.13 ± 0.02 a	54.55 ± 3.55 ab
	MC-25	0.43 ± 0.01 a	79.59 ± 5.58 a	pH- 3	MC-0	0.11 ± 0.01 a	49.20 ± 1.47 d
pH- 4	MC-0	0.41 ± 0.05 a	78.15 ± 6.86 a		MC-25	0.12 ± 0.02 a	51.39 ± 2.75 abcd
	MC-25	0.44 ± 0.05 a	84.58 ± 7.45 a	pH- 4	MC-0	0.13 ± 0.03 a	49.54 ± 1.98 cd
pH- 5	MC-0	0.42 ± 0.03 a	78.79 ± 4.25 a		MC-25	0.13 ± 0.02 a	51.32 ± 2.65 abcd
	MC-25	0.44 ± 0.02 a	83.68 ± 6.92 a	pH- 5	MC-0	0.15 ± 0.03 a	49.24 ± 2.1 cd
Analyses of variance		F-values	F-values	Analyses of variance		F-values	F-values
pH		2.06	0.38	pH		0.89	1.74
MC		0	1.07	MC		0.29	10.72 ***
pH × MC		0.37	0.32	pH × MC		1.00	0.21
Canterbury potato trial Treatments		Soil Cd (mg kg^{-1})	Soil Zn (mg kg^{-1})	Canterbury wheat trial Treatments		Soil Cd (mg kg^{-1})	Soil Zn (mg kg^{-1})
pH- 1	MC-0	0.16 ± 0.08 a	59.40 ± 0.99 bc	pH- 1	MC-0	0.23 ± 0.03 a	50.69 ± 1.04 abc
	MC-25	0.17 ± 0.07 a	61.46 ± 2.39 a	pH- 2	MC-0	0.17 ± 0.03 ab	48.12 ± 2.14 c
	MC-50	0.13 ± 0.01 a	63.24 ± 1.52 a		MC-25	0.21 ± 0.06 ab	51.98 ± 3.17 abc
pH- 2	MC-0	0.13 ± 0.03 a	58.50 ± 2.20 bc		MC-50	0.17 ± 0.04 c	53.90 ± 4.37 a
	MC-25	0.13 ± 0.02 a	60.94 ± 2.66 abc	pH- 3	MC-0	0.28 ± 0.12 a	48.67 ± 2.31 bc
pH- 3	MC-0	0.12 ± 0.02 a	60.76 ± 1.30 abc		MC-25	0.22 ± 0.03 ab	52.33 ± 2.68 abc
	MC-25	0.15 ± 0.07 a	61.38 ± 2.04 ab	pH- 4	MC-0	0.21 ± 0.04 ab	49.91 ± 1.76 abc
pH- 4	MC-0	0.16 ± 0.07 a	58.42 ± 2.92 c		MC-25	0.23 ± 0.02 ab	53.17 ± 3.37 ab
	MC-25	0.17 ± 0.07 a	60.15 ± 3.09 ab	pH- 5	MC-0	0.19 ± 0.02 ab	50.94 ± 0.42 abc
pH- 5	MC-0	0.12 ± 0.01 a	57.89 ± 2.01 c		MC-25	0.20 ± 0.01 ab	51.20 ± 0.83 abc
Analyses of variance		F-values	F-values	Analyses of variance		F-values	F-values
pH		0.53	3.02 *	pH		2.37	0.17
MC		0.88	6.69 **	MC		1.42	6.03 **
pH × MC		0.3	0.57	pH × MC		0.29	0.68

Data in the table shows the means of three replicates ± standard error, and same letter between treatments in each column stands non significance at the 5% level. Significance levels of lime, compost and the interaction Lime × compost are indicated: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

Table C2 The yield of potato in Pukekohe and Canterbury potato trial, and wheat grain in wheat trial

Pukekohe potato trial Treatments		Yield ($t\ ha^{-1}$)	Canterbury potato trial Treatments		Yield ($t\ ha^{-1}$)	Canterbury wheat trial Treatments		Yield ($t\ ha^{-1}$)
pH- 1	MC-0	54.9 ± 1.50 a	pH- 1	MC-0	55.59 ± 2.36 a	pH- 1	MC-0	6.17 ± 1.37 a
pH- 2	MC-0	47.68 ± 2.34 a		MC-25	53.96 ± 5.00 a	pH- 2	MC-0	6.80 ± 1.58 a
	MC-25	50.92 ± 2.39 a		MC-50	61.84 ± 3.54 a		MC-25	6.68 ± 1.26 a
	MC-50	44.65 ± 2.30 a	pH- 2	MC-0	58.50 ± 4.09 a		MC-50	7.10 ± 1.32 a
pH- 3	MC-0	46.97 ± 2.80 a		MC-25	59.58 ± 2.21 a	pH- 3	MC-0	6.79 ± 0.80 a
	MC-25	46.66 ± 1.09 a	pH- 3	MC-0	48.71 ± 2.62 a		MC-25	8.36 ± 0.96 a
pH- 4	MC-0	43.35 ± 4.43 a		MC-25	58.50 ± 2.67 a	pH- 4	MC-0	5.58 ± 1.52 a
	MC-25	47.55 ± 2.31 a	pH- 4	MC-0	58.79 ± 2.85 a		MC-25	6.14 ± 0.64 a
pH- 5	MC-0	46.31 ± 2.83 a		MC-25	48.75 ± 3.00 a	pH- 5	MC-0	6.78 ± 0.92 a
	MC-25	45.78 ± 1.16 a	pH- 5	MC-0	53.96 ± 2.76 a		MC-25	6.31 ± 1.35 a
Analyses of variance		F-values	Analyses of variance		F-values	Analyses of variance		F-values
pH		0.06	pH		0.36	pH		0.69
MC		0.23	MC		0.23	MC		0.88
pH × MC		0.70	pH × MC		0.04 *	pH × MC		0.84

Data in the table shows the means of three replicates ± standard error, and same letter between treatments in each column stands non significance at the 5% level. Significance levels of lime, compost and the interaction Lime × compost are indicated: * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

Direction of cultivation (45 m)	Block 1					Block 1					Block 1				
	Buffer					Buffer					Buffer				
	Buffer	25. T6	Buffer	26. T9	Buffer	Buffer	27. T4	Buffer	28. T5	Buffer	Buffer	29. T1	Buffer	30. T7	Buffer
		24. T10		23. T5			22. T2		21. T6			20. T6		19. T9	
		13. T7		14. T3			15. T10		16. T1			17. T8		18. T4	
		12. T4		11. T2			10. T3		9. T8			8. T5		7. T3	
		1. T8		2. T1			3. T9		4. T7			5. T2		6. T10	
	Buffer					Buffer					Buffer				

	E	
N		S
	W	

Figure C1A. The layout of potato trial in Canterbury

Figure C1B. the setup of potato trial

Figure C1B. sowing potatoes in Oct 20106

Figure C1 The design and management of potato trial

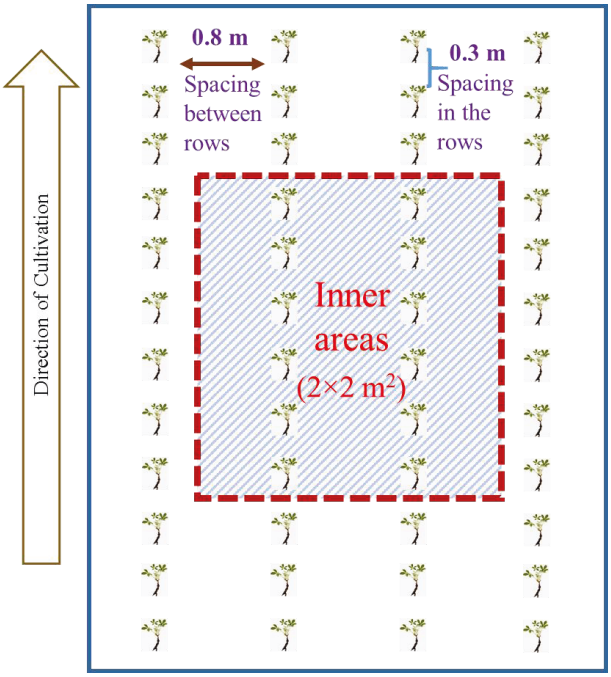

Figure C2 Trial plot design potato field trials

Direction of cultivation (45 m)		Block 1	Block 2	Block 3	
		Buffer	Buffer	Buffer	
		30. T6	11. T4	10. T1	
		29. T10	12. T2	9. T6	
		28. T7	13. T10	8. T8	
	Buffer	27. T4	14. T3	7. T5	Buffer
		26. T8	15. T9	6. T2	
		25. T9	16. T5	5. T7	
		24. T5	17. T6	4. T9	
		23. T3	18. T1	3. T4	
		22. T2	19. T8	2. T3	
		21. T1	20. T7	1. T10	
		Buffer	Buffer	Buffer	

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Figure C3A. the layout of wheat trial

Figure C3B. the sowing in wheat trial

Figure C3C. the growth of wheat in Aug 2016

Figure C3 The design and management of wheat and spinach trials

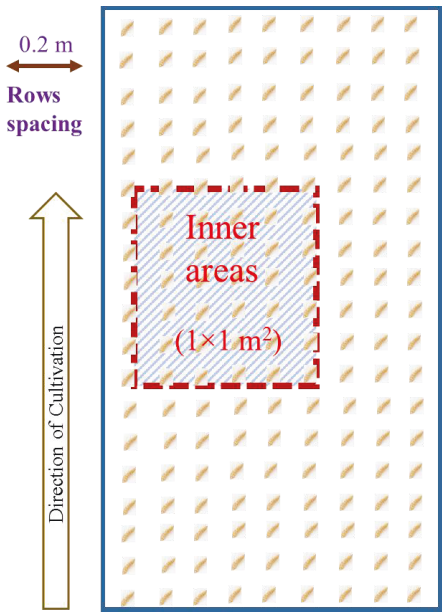

Figure C4 Trial plot design wheat field trials

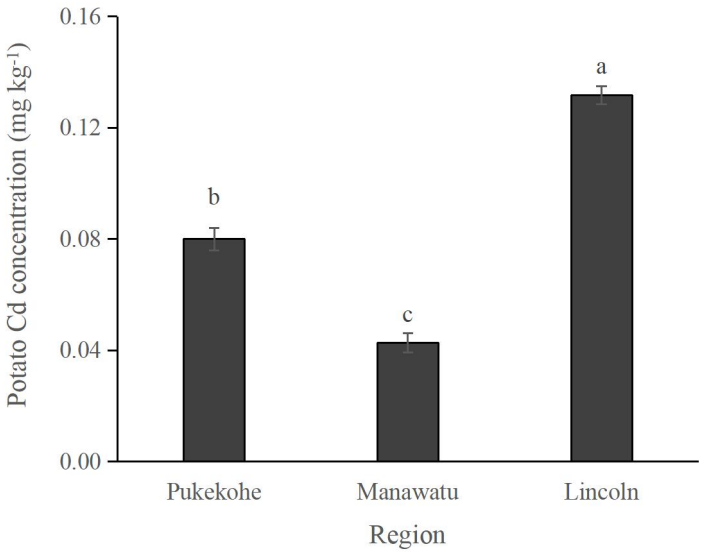

Figure C5 The Cd concentration in potato tuber between different trials. Data in the table shows the means of three replicates ± standard error, and same letter stands non significance at the 5% level.

Appendix D

Supplementary information in Chapter 5

Table D1 The model parameters used for soil Cd concentration prediction in some studies

Countries	Cd mass balance	Basic description model (parameters)
Australia (de Vries & McLaughlin, 2013)	Cd input	Fertiliser application: Cd concentration in P fertiliser (mg kg^{-1}), the P application rate (kg ha^{-1}) Atmospheric deposition (g ha^{-1}) Biosolids: application rate (t ha^{-1}), Cd concentration in biosolids (mg kg^{-1}) Irrigation water: irrigation rate, m^3 ha^{-1} yr^{-1}
	Cd output	Leaching: Cd concentration in soil solution (μg L^{-1}), annual precipitation (m), irrigation (m), surface runoff (m) and actual evapotranspiration for that cultivation depth (m) which varied between farming purposes Crop offtake: crop yield (kg ha^{-1}), the concentration of Cd in crops (mg kg^{-1}), soil pH, soil clay (%), soil organic C (%)
Canada (Sheppard et al., 2009)	Cd input	Fertiliser application: Cd concentration in N, P micronutrient fertiliser (mg kg^{-1}), the application rate of N, P and micronutrient fertiliser (kg ha^{-1}) Atmospheric deposition (g ha^{-1}) Biosolids: application rate (yr^{-1}), Cd concentration in biosolids (mg kg^{-1}), production of sludge (t $person^{-1}$) Manure: manure application return rate (yr^{-1}), manure production (kg $animal^{-1}$)
	Cd output	Leaching: solid/liquid Cd partition coefficient (K_{ds}) (L kg^{-1}), water deep leaching rate (m yr^{-1}), background Cd concentration (mg kg^{-1}), soil depth (0.3 m) Crop off-take: crop yield (kg ha^{-1}), feed intake (kg $animal^{-1}$), plant/soil Cd concentration ratios(TF), background Cd concentration (mg kg^{-1})
The Europe (Six & Smolders, 2014)	Cd input	Fertiliser application: Cd concentration in P fertiliser (mg kg^{-1}), the P application rate (kg ha^{-1}) Atmospheric deposition (g ha^{-1}) Biosolids or animal feeds: application rate (t ha^{-1}), Cd concentration in biosolids (mg kg^{-1})
	Cd output	Leaching: the soil/water partitioning coefficient (*K*d, L kg^{-1}), annual precipitation excess (m yr^{-1}), bulk density (ρ, kg m^{-3}) and soil depth (*d*, m), the modelled soil depth (0.2 m). Crop offtake: crop yield (kg ha^{-1}), plant/soil Cd concentration ratios (TF), background Cd concentration (mg kg^{-1})

Table D2 The precipitation excess in four regions

Region	Agent number	Network number	Latitude	Longitude	Year period	Rainfall (m)	Run-off (m)	Evaporation (m)	Precipitation excess (m)
Canterbury	24120	H3256F	- 43.531	172.608	2003-2017	0.63	0.13	0.89	0.19
	26607	H32063	- 43.070	172.653	2007-2017	0.61	0.07	1.13	0.18
	26170	H31983	- 43.905	171.805	2006-2017	0.72	0.15	0.91	0.21
	5086	H41325	- 44.305	171.221	2003-2017	0.54	0.05	0.76	0.19
	11234	G22582	- 42.534	172.851	2003-2017	0.98	0.37	0.81	0.23
					Mean				0.20
Waikato	26117	C75734	- 37.776	175.305	2006-2017	1.13	0.44	0.90	0.24
	1547	B75362	- 37.371	175.684	2003-2017	1.17	0.45	0.89	0.27
	25643	C85977	- 38.975	175.791	2003-2017	1.36	0.62	0.85	0.29
	23899	C85316	- 38.333	175.153	2004-2016	1.30	0.60	0.77	0.29
	12428 *	B76838	- 37.822	176.324	2003-2017	1.75	0.87	0.83	0.45
					Mean				0.31
Bay of Plenty	12428 *	B76838	- 37.822	176.324	2003-2017	1.75	0.87	0.83	0.45
	1770	B86133	- 38.106	176.315	2003-2017	1.21	0.49	1.02	0.28
	1673	B76995	- 37.925	176.919	2003-2017	1.36	0.65	0.90	0.29
					Mean				0.34
Southland	11104	I68435	- 46.411	168.318	2003-2017	1.08	0.36	0.79	0.21
	5430	I57563	- 45.533	167.642	2003-2017	1.05	0.40	0.75	0.22
	5778	I68182	- 46.115	168.887	2003-2017	0.91	0.21	0.80	0.23
					Mean				0.22
					Total mean				0.26

* Climatic information in station 12428 which locates closely to the boundary between Waikato and Bay of plenty was applied twice.

Table D3 Input data of SCM model and CadBal in dryland (the Winchmore irrigation trial)

Input	Unit	(McDowell, 2012)	(Salmanzadeh et al., 2017a)	This study (SCM model)
Farm type		Sheep/beef	Sheep/beef	Sheep/beef
Pasture yield	kg DM ha^{-1} $year^{-1}$	Annual data from Rickard and McBride (1986); (Rickard & McBride, 1987)	6442 (average of pasture yield in Smith et al. (2012)	Annual data (1952-2010) from Smith et al. (2012) and 5039 (average value from 1952 to 2010) for 2011-2030
Precipitation excess	m yr^{-1}	ns	ns	Annual data calculated from NIWA (Table S10)
Pasture Cd	g	Cd uptake = yield (kg ha^{-1}) × (0.368 × 0.658 × $0.00158^{[Cd]n}$) / 1000	Cd uptake = yield (kg ha^{-1}) × (0.368 × 0.658 × $0.00158^{[Cd]n}$) / 1000	Crops offtake model Eq. (6)
Soil pH		ns	ns	5.75 (1952 - 1994) [a]; 5.57 (1995 - 2009); 5.20 (2010 - 2030)
Soil OC	%	ns	ns	Annual data from Schipper et al. (2013) and 5.26 (2007-2030) (McDowell, 2010)
Sediment yield (erosion)	kg ha^{-1} $year^{-1}$	50	50	50
Soil group		Yellow-grey earth	Yellow-grey earth	Yellow-grey earth
Bulk density	g cm^{-3}	1.01	1.01	1.21 (McDowell & Rowley, 2008; Schipper et al., 2013); 1.06 (Srinivasan & McDowell, 2009)
Sample depth	cm	7.5	7.5	7.5
Initial soil Cd	mg kg^{-1}	0.06	0.02	0.06
P fertiliser rate	kg P ha^{-1} yr^{-1}	24	24	24
P fertiliser Cd	mg kg^{-1}	345 (1952-1968)	345 (1952-1968)	345 (1952-1968)
		325 (1968-1975)	325 (1968-1975)	325 (1968-1975)
		155 (1975-1983)	155 (1975-1983)	155 (1975-1983)
		325 (1983-1996)	325 (1983-1996)	325 (1983-1996)
		175 (1996-1999)	275 (1998-2000)	275 (1998-2000)
		70 (1999 -)	281 (2000-2001)	281 (2000-2001)
			152 (2001-2005)	152 (2001-2005)
			219 (2005-2007)	219 (2005-2007)
			243 (2007-2011)	243 (2007-2011)
			161 (2011-2013)	161 (2011-2013)
			215 (2013-2015)	215 (2013-2015)
			86 (2015-2030)	86 (2015-2030)
Leaching loss	g ha^{-1} $year^{-1}$	1.6	1.6 (1952-2000) & 3.2 (post-2000)	Leaching model Eq. (7)
Atmospheric deposition	g ha^{-1} $year^{-1}$	0.17 from Gray et al. (2003a)	0.17	0.17

[a] Lime was applied in dryland trial in 1948 and 1965 to maintain soil pH at 5.5 to 6.0 (McDowell, 2012). Because no soil pH was monitored over time, soil pH was rough estimated at 5.75 from 1952 to 1994. Value of 5.57 was from Fraser et al. (2012), 5.20 from (McDowell, 2010).

Table S4 Input data of the SCM model

Year	Dryland			Irrigation (15% v/v)						
	Precipitation excess (m)	Soil pH	Soil OC (%)	Precipitation excess (m)	Soil pH [a]			Soil OC [b] (%)		
		24 kg P	24 kg P		0 kg P	17 kg P	34 kg P	0 kg P	17 kg P	34 kg P
1952	0.21	5.75	2.66	0.46	6.20	6.20	6.20	2.66	2.66	2.66
1953	0.28	5.75	2.79	0.48	6.20	6.20	6.20	2.69	2.74	2.67
1954	0.29	5.75	2.92	0.51	6.20	6.20	6.20	2.74	2.80	2.69
1955	0.19	5.75	3.05	0.34	6.20	6.20	6.20	2.79	2.87	2.70
1956	0.34	5.75	3.18	0.57	6.20	6.20	6.20	2.83	2.92	2.72
1957	0.20	5.75	3.31	0.46	6.20	6.20	6.20	2.89	3.02	2.73
1958	0.22	5.75	3.44	0.44	6.33	6.32	6.28	2.75	3.13	2.95
1959	0.28	5.75	3.57	0.49	6.17	6.12	6.17	2.84	3.27	2.98
1960	0.17	5.75	3.70	0.40	6.17	6.05	6.10	2.87	3.36	3.02
1961	0.20	5.75	3.83	0.45	5.96	5.95	5.87	2.91	3.47	3.08
1962	0.23	5.75	3.87	0.48	6.10	6.10	6.10	2.96	3.59	3.09
1963	0.18	5.75	3.93	0.37	5.93	5.93	6.00	3.00	3.68	3.13
1964	0.11	5.75	3.98	0.27	6.04	5.99	6.03	3.04	3.75	3.21
1965	0.22	5.75	4.03	0.44	6.01	5.93	6.00	3.09	3.82	3.26
1966	0.23	5.75	4.07	0.45	5.90	5.91	5.93	3.16	3.87	3.29
1967	0.21	5.75	4.10	0.47	5.98	5.98	6.00	3.17	3.89	3.34
1968	0.24	5.75	4.13	0.45	6.12	6.01	6.05	3.22	3.91	3.39
1969	0.10	5.75	4.14	0.36	6.18	6.06	6.00	3.25	3.93	3.40
1970	0.22	5.75	4.16	0.47	6.05	6.05	6.00	3.26	3.93	3.44
1971	0.15	5.75	4.15	0.39	5.96	5.96	5.90	3.27	3.93	3.48
1972	0.21	5.75	4.15	0.45	5.98	5.88	5.90	3.29	3.93	3.48
1973	0.14	5.75	4.16	0.33	6.45	6.43	6.40	3.30	3.92	3.48
1974	0.20	5.75	4.15	0.45	6.58	6.54	6.53	3.32	3.92	3.49
1975	0.31	5.75	4.15	0.56	6.37	6.34	6.30	3.33	3.91	3.50
1976	0.20	5.75	4.16	0.42	6.39	6.33	6.37	3.37	3.91	3.52
1977	0.19	5.75	4.16	0.39	6.20	6.20	6.18	3.38	3.90	3.54
1978	0.24	5.75	4.15	0.46	6.13	6.03	6.10	3.41	3.90	3.55
1979	0.23	5.75	4.15	0.49	6.07	6.08	6.00	3.43	3.91	3.56
1980	0.20	5.75	4.16	0.43	6.00	5.83	5.90	3.42	3.91	3.57
1981	0.16	5.75	4.17	0.38	6.15	6.00	6.00	3.45	3.92	3.59
1982	0.20	5.75	4.18	0.44	6.05	5.97	6.03	3.45	3.92	3.58
1983	0.24	5.75	4.20	0.44	6.01	5.88	5.97	3.46	3.91	3.59
1984	0.27	5.75	4.22	0.50	5.97	5.88	5.90	3.50	3.91	3.60
1985	0.27	5.75	4.23	0.54	5.90	5.86	5.83	3.59	3.89	3.61
1986	0.33	5.75	4.53	0.54	6.00	5.85	5.95	3.57	3.88	3.64
1987	0.33	5.75	4.28	0.56	5.90	5.96	5.87	3.60	3.90	3.67
1988	0.19	5.75	4.32	0.39	5.84	5.83	5.83	3.65	3.92	3.68
1989	0.26	5.75	4.36	0.46	5.91	5.80	5.85	3.79	3.94	3.71
1990	0.21	5.75	4.38	0.44	5.97	5.81	5.88	3.77	3.96	3.73
1991	0.27	5.75	4.54	0.50	5.90	5.86	5.75	3.78	3.98	3.77

Year	Dryland			Irrigation (15% v/v)						
	Precipitation excess (m)	Soil pH	Soil OC (%)	Precipitation excess (m)	Soil pH [a]			Soil OC [b] (%)		
		24 kg P	24 kg P		0 kg P	17 kg P	34 kg P	0 kg P	17 kg P	34 kg P
1992	0.19	5.75	4.48	0.44	5.81	5.79	5.67	3.83	4.00	3.79
1993	0.22	5.75	4.52	0.51	5.75	5.69	5.68	3.95	4.02	3.82
1994	0.22	5.75	4.54	0.45	5.79	5.70	5.79	3.89	4.04	3.85
1995	0.21	5.57	4.57	0.49	5.76	5.77	5.70	3.92	4.06	3.86
1996	0.19	5.57	4.58	0.46	5.79	5.69	5.63	3.94	4.08	3.88
1997	0.26	5.57	4.59	0.50	5.79	5.64	5.67	3.95	4.10	3.89
1998	0.18	5.57	4.58	0.37	5.81	5.60	5.72	3.96	4.12	3.89
1999	0.23	5.57	4.57	0.48	5.80	5.70	5.70	3.98	4.15	3.90
2000	0.27	5.57	4.56	0.52	5.81	5.71	5.67	3.99	4.17	3.90
2001	0.17	5.57	4.56	0.41	5.78	5.65	5.71	4.00	4.19	3.91
2002	0.30	5.57	4.55	0.51	5.79	5.71	5.68	4.02	4.21	3.93
2003	0.24	5.57	4.71	0.45	5.79	5.67	5.65	4.03	4.23	3.94
2004	0.30	5.57	4.87	0.57	5.75	5.60	5.65	4.05	4.25	3.98
2005	0.19	5.57	5.03	0.42	5.75	5.60	5.65	4.08	4.27	4.01
2006	0.30	5.57	5.19	0.57	5.75	5.60	5.65	4.10	4.29	4.06
2007	0.19	5.57	5.26	0.40	5.75	5.60	5.65	4.14	4.31	4.12
2008	0.23	5.57	5.26	0.45	5.75	5.60	5.65	4.20	4.33	4.18
2009	0.26	5.57	5.26	0.44	5.72	5.60	5.65	4.28	4.35	4.27
2010	0.21	5.20	5.26	0.38	5.50	5.40	5.50	4.18	4.35	4.25
2011	0.24	5.20	5.26	0.45	5.65	5.50	5.65	4.18	4.35	4.25
2012	0.27	5.20	5.26	0.49	5.65	5.50	5.65	4.18	4.35	4.25
2013	0.38	5.20	5.26	0.47	5.65	5.50	5.65	4.18	4.35	4.25
2014	0.13	5.20	5.26	0.35	5.65	5.50	5.65	4.18	4.35	4.25
2015	0.17	5.20	5.26	0.38	5.65	5.50	5.65	4.18	4.35	4.25
2016	0.19	5.20	5.26	0.42	5.65	5.50	5.65	4.18	4.35	4.25
2017	0.17	5.20	5.26	0.26	5.80	5.48	5.55	4.18	4.35	4.20
2018	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2019	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2020	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2021	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2022	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2023	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2024	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2025	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2026	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2027	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2028	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2029	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20
2030	0.23	5.20	5.26	0.45	5.80	5.48	5.55	4.18	4.35	4.20

[a] Soil pH data in fertiliser trial were from Goh and Condron (1989), Fraser et al. (2011), McDowell (2010), and Wakelin et al. (2017).
[b] Soil OC data sourced from Nguyen and Goh (1990), Metherell (2003), McDowell (2010), Schipper et al. (2013), and Wakelin et al. (2017).

Table D5 The distribution fitting results of four main soil parameters

Soil variables	Distribution	Distribution parameters				Estimator of fitting results		
		Median of modelling data [a]	Std.e	Standard deviation	Std.e	Log-likelihood	AIC	BIC
pH	Log-normal	1.78 (5.93)	0.005	0.09	0.003	-350	705	713
	Normal	5.93	0.027	0.55	0.019	-345	694	702
	Weibull	11.41 (5.99)	0.405	6.18	0.028	-361	727	735
OC (%)	Log-normal	1.71 (5.53)	0.027	0.56	0.019	-1064	2131	2139
	Normal	6.48	0.223	4.56	0.157	-1230	2464	2472
	Weibull	1.62 (5.81)	0.051	7.28	0.233	-1121	2246	2254
Bulk density ($g\ cm^{-3}$)	Log-normal	-0.04 (0.96)	0.013	0.27	0.009	-27	58	66
	Normal	0.99	0.012	0.25	0.009	-13	29	37
	Weibull	4.41 (1.00)	0.166	1.09	0.013	-13	31	39
Cd ($mg\ kg^{-1}$)	Log-normal	-1.17 (0.31)	0.014	0.90	0.010	-538	1080	1092
	Normal	0.44	0.006	0.36	0.004	-1513	3030	3042
	Weibull	1.28 (0.36)	0.016	0.48	0.006	-514	1031	1044

[a] The numbers in brackets are the median valued transferred from each distribution.

Table D6 The parameters for Monte Carlo simulation of soil types (dry-stock soils)

Parameter	Organic		Pumice		Sedimentary		Volcanic		Others [@]	
	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation
Soil Cd (mg kg^{-1})	0.79 [b]	0.89	0.53 [b]	0.63	0.21 c	0.72	0.81 [b]	0.93	0.29 [b]	0.40
Soil pH	6.11 [c]	0.06	5.70 [c]	0.06	5.91 [a]	0.57	5.99 [c]	0.09	5.74 [a]	0.71
Soil OC (%)	20.29 [c]	0.56	7.44 [a]	2.30	4.35 [c]	0.47	7.94 [b]	9.30	5.90 [a]	2.15
Soil Bulk density (g cm^{-3})	0.60 [c]	0.33	0.70 [a]	0.11	1.12 [a]	0.21	0.85 [a]	0.19	1.02 [a]	0.18
Atmospheric deposition (g ha^{-1}) [d]	0.2									
P input kg ha^{-1} [e]	25 ± 2.5									
Cd plant transfer factor [f]	Organic - 0.378; Pumice- 0.364; Sedimentary - 1.215; Volcanic - 0.426; Others- 0.954									
Plant yield (kg ha^{-1}) [g]	7,000 ± 1,400									
Precipitate excess (m) [g]	0.26 ± 0.05									
irrigation rate (m)	0									
Cd in P mg kg^{-1}	100, 184, 280									

[a] Normal distribution; [b] Weibull distribution; [c] Log-normal distribution;

[d] Atmospheric Cd deposition rate was the national mean value of Gray et al. (2003a);

[e] Annual P input was assumed to have 10% variation due to potential natural or human factors.

[f] Cd soil-plant transfer coefficients were summarised from Cd research in NZ (Table 2).

[g] Annual plant yield were assumed to be same between soil orders with 20% variation according to the report of Moot et al. (2009); precipitation excess was also assumed with 20% variation.

[@] Soils not belonging to the four main soil orders were considered *Others* (Roberts & Morton, 2009).

Table D7 The parameters for Monte Carlo simulation of land-use

Parameter	Dairy[@]		Drystock[@]		Cropping	
	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation
Soil Cd (mg kg^{-1})	0.52 [b]	0.65	0.24 [c]	0.81	0.21 [c]	0.67
Soil pH	5.99 [c]	0.05	5.81 [c]	0.07	6.30 [c]	0.07
Soil OC (%)	7.31 [c]	0.48	5.93 [c]	0.46	3.86 [c]	0.52
Soil Bulk density (g cm^{-3})	0.89 [a]	0.20	0.97 [a]	0.21	1.15 [b]	1.23
Atmospheric deposition (g ha^{-1})	0.2					
Cd in P (mg kg^{-1})	184					
P input (kg ha^{-1})	45 ± 4.5		25 ± 2.5		Potato : 75 ± 7.5; Onion : 60 ± 7.5; Wheat : 50 ± 7.5	
Cd plant transfer factor [d]	Ryegrass : 0.43; Clover : 0.32; Chicory : 2.68; Plantain : 1.22				Potato : 0.622; Onion : 0.246; Wheat : 0.325	
Plant yield (kg ha^{-1}) [e]	16500 - 17500		7,000 ± 1,400		Potato : 41800 - 60400; Onion : 35000 - 38400; Wheat : 9000 - 11700	
Precipitation excess (m)	0.26 ± 0.05					
Irrigation rate (m)	0, 0.30, 0.60		0, 0.15, 0.30		0, 0.150, 0.30	

[a] Normal distribution; [b] Weibull distribution; [c] Log-normal distribution;

[d] Cd soil-plant transfer coefficients were summarised from Cd research in NZ (Table 3).

[e] Dairy pasture yield derived from Clark et al. (2007), drystock from Moot et al. (2009), potato & onion yield from Ministry for Primary Industries (2009) and wheat from FAR Cultivar Evaluation (2017). The moisture content of potato was assumed to be 81.9%, 88.9 % for onion and 10% for wheat grain.

[@] Pasture was assumed to be composed by ryegrass (*Lolium perenne*), white clover (*Trifolium subterraneum L.*), plantain (*Plantago lanceolata*) and chicory (C*ichorium intybus*) at the ratio of 7:2:0.5:0.5.

Table D8 Model parameters used to estimate soil Cd accumulation in Waikato region

Parameter	Dairy		Drystock		Cropping	
	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation
Soil Cd (mg kg^{-1})	0.83 [b]	0.92	0.57 [b]	0.74	0.64 [a]	0.25
Soil pH	6.05 [c]	0.06	5.89 [a]	0.41	6.28 [a]	0.54
Soil OC (%)	8.58 [c]	0.59	8.99 [a]	3.01	5.07 [a]	1.69
Soil Bulk density (g cm^{-3})	0.79 [a]	0.18	0.79 [c]	0.21	0.90 [c]	0.20
Atmospheric deposition [d] (g ha^{-1})	0.27					
Cd in P (mg kg^{-1})	184					
P input (kg ha^{-1})	45 ± 4.5		35 ± 2.5		Potato : 90 ± 9.0, Onion : 80 ± 8.0;	
	35 ± 3.5		25 ± 2.5		Potato : 70 ± 7.0, Onion : 60 ± 6.0;	
	25 ± 2.5		15 ± 2.5		Potato : 50 ± 5.0, Onion : 40 ± 4.0;	
Cd plant transfer factor [e]	Ryegrass : 0.18;		Ryegrass : 0.18;		Potato : 0.17;	
	Clover : 0.09;		Clover : 0.09;		Onion : 0.09	
	Chicory : 0.84;		Chicory : 0.84;			
	Plantain : 0.58		Plantain : 0.58			
Plant yield [f] (kg ha^{-1})	16,500 ± 3,300		12,000 ± 2,400		Potato : 41800 ± 8,360;	
					Onion : 35000 ± 7,000	
Precipitation excess (m)	0.31 ± 0.062					
Irrigation rate (m)	0		0		0.10	

[a] Normal distribution; [b] Weibull distribution; [c] Log-normal distribution;

[d] Atmospheric Cd deposition rate was from site F in Gray et al. (2003a);

[e] Cd soil-plant transfer coefficients were derived from Cavanagh et al. (2016) in Waikato region.

[f] Dairy pasture yield (dry weight) derived from Clark et al. (2007), drystock (dry weight) from Moot et al. (2009), and potato & onion yield (fresh weight) from Ministry for Primary Industries (2009). The moisture content of potato was assumed to be 81.9% and 88.9 % for onion.

Table D9 Model parameters used to estimate soil Cd accumulation in Canterbury region

Parameter	Dairy		Drystock		Cropping	
	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation	Median of modelling data	Standard deviation
Soil Cd (mg kg^{-1})	0.22 [c]	0.50	0.15 [c]	0.36	0.19 [c]	0.45
Soil pH	5.79 [a]	0.27	5.78 [a]	0.31	5.83 [a]	0.32
Soil OC (%)	3.36 [a]	0.81	3.15 [a]	0.63	2.70 [a]	0.48
Soil Bulk density (g cm^{-3})	1.24 [a]	0.11	2.70 [a]	0.48	1.20 [a]	0.09
Atmospheric deposition [d] (g ha^{-1})	0.17					
Cd in P (mg kg^{-1})	184					
P input (kg ha^{-1})	55 ± 5.5		35 ± 2.5		Potato : 90 ± 9.0, Onion : 80 ± 8.0;	
	40 ± 4.0		25 ± 2.5		Potato : 70 ± 7.0, Onion : 60 ± 6.0;	
	25 ± 2.5		15 ± 2.5		Potato : 50 ± 5.0, Onion : 40 ± 4.0;	
Cd plant transfer factor [e]	Ryegrass : 0.33; Clover : 0.15;				Potato : 1.44; Onion : 0.26;	
	Chicory : 1.78; Plantain : 2.95				Wheat : 0.33	
Plant yield [f] (kg ha^{-1})	Irrigation:18,000 ± 3,600;		Irrigation:10,200 ± 1,000;		Potato : 60,400 ± 12,080;	
	Non - irrigation: 9,000 ± 1,800		Non - irrigation: 5,900 ± 1,100		Onion : 38,400 ± 7,680;	
					Wheat : 9,000 - 11,700	
Precipitation excess (m)	0.20 ± 0.04					
Irrigation rate (m)	0.54		0.26		Potato,0.35; onion, 0.30; wheat, 0.20	

[a] Normal distribution; [b] Weibull distribution; [c] Log-normal distribution;

[d] Atmospheric Cd deposition rate was from site B in Gray et al. (2003a);

[e] Cd soil-plant transfer coefficients were derived from Cavanagh et al. (2016) in Canterbury region.

[f] Dairy pasture yield (dry weight) derived from Clark et al. (2007), drystock (dry weight) from Moot et al. (2009), potato & onion yield (fresh weight) from Ministry for Primary Industries (2009) and wheat (fresh weight) from FAR Cultivar Evaluation (2017). The moisture content of potato was assumed to be 81.9%, 88.9 % for onion and 10% for wheat grain.

Table D10 Experimentally determined and calculated Kd values for Cd in NZ soils, and model estimates of annual changing soil Cd in 25 years at the application rate of 25 kg P ha^{-1} (184 mg Cd kg^{-1} P)

Soil order	K_d Cd values (L kg^{-1})	K_d from model (L kg^{-1})		P input	Air input	plant uptake	Leaching	Annual change rate
		Median	5^{th} - 95^{th} percentile	(μg kg^{-1})	(μg kg^{-1})	(μg kg^{-1})	(μg kg^{-1})	(μg kg^{-1})
Organic	ns [a]	1649	593 - 4644	10.18	0.44	0.73	2.90	6.45
Pumice	599 [b]	442	195- 1008	8.79	0.38	0.40	6.11	2.66
Sedimentary	390 [b]	378	109 - 1252	5.47	0.24	0.39	2.16	2.94
Volcanic	680 [b]	626	214 - 1970	7.20	0.31	0.55	5.00	1.99
Others	ns [a]	365	106 - 1601	6.06	0.26	0.42	3.00	2.70

[a] Data is not available in NZ;

[b] K_d values represent Cd_S: Cd_{sol} ratio, in which data of soils top 5 cm and 5-10 cm are from Gray et al. (2003b). The data about Pumice soil 1 in the study of Gray et al. (2003b) was excluded due to considerable OC content.

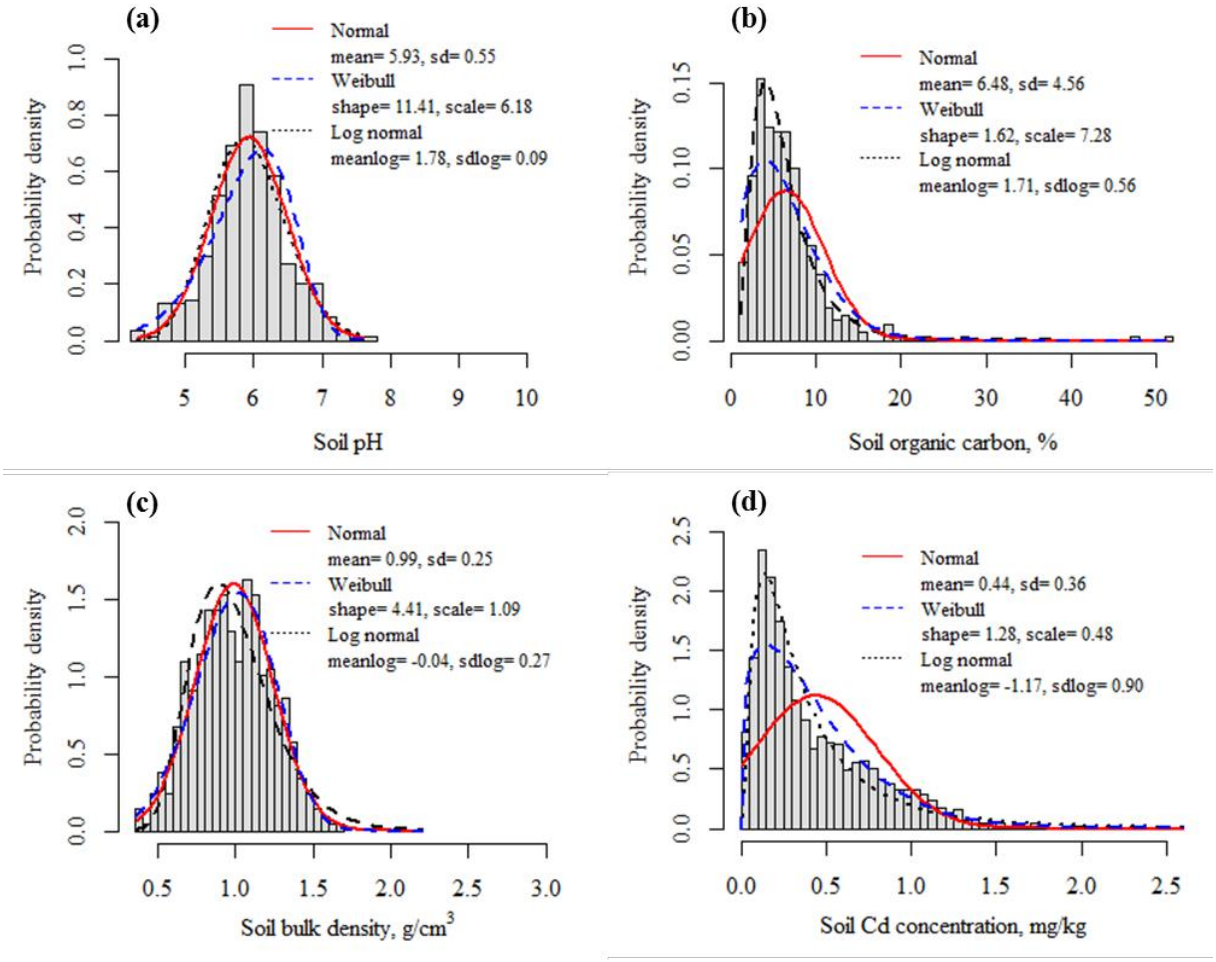

Figure D1. The distribution of four soil parameters, soil pH (a), OC content (b), bulk density (c) and Cd concentrations (d).

Appendix E

Supplementary information in Chapter 6

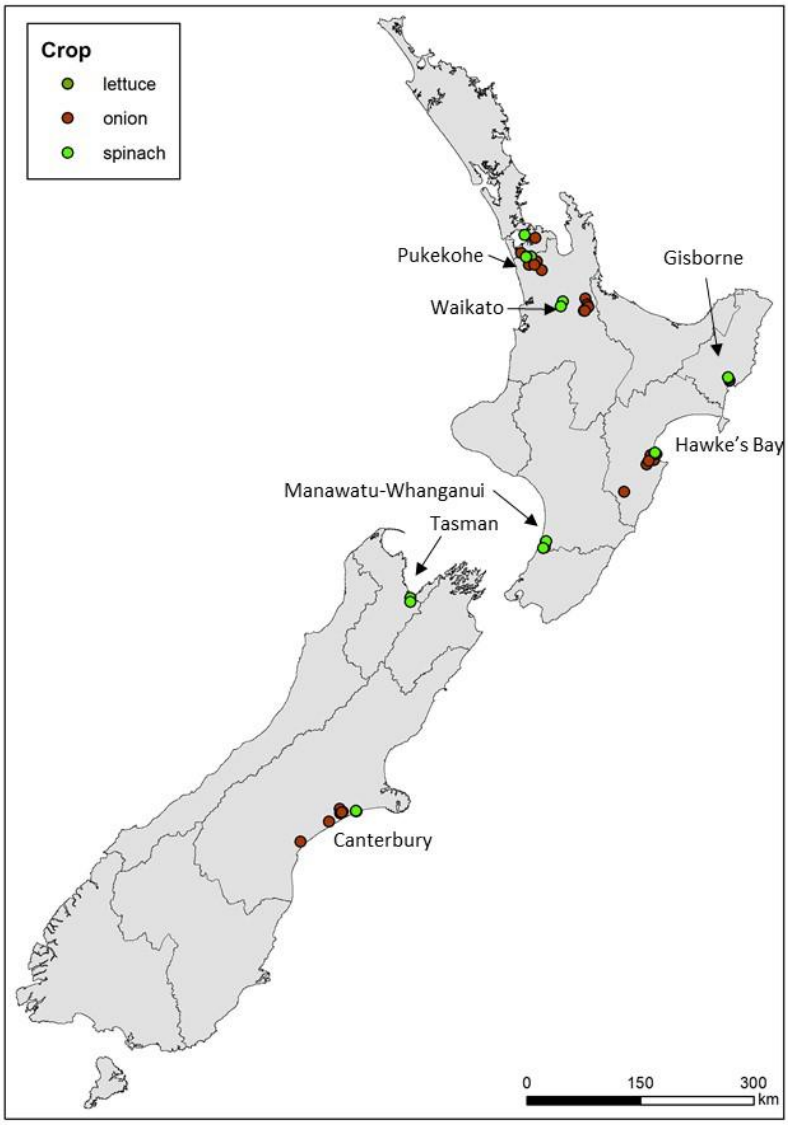

Figure E1 General location of sampling sites for lettuce, onions and spinach. Lines show regional boundaries, with the exception of Pukekohe the names shown are the associated region names. Pukekohe is an important horticultural growing area of New Zealand that spans two regions and so is retained as a separately identified region

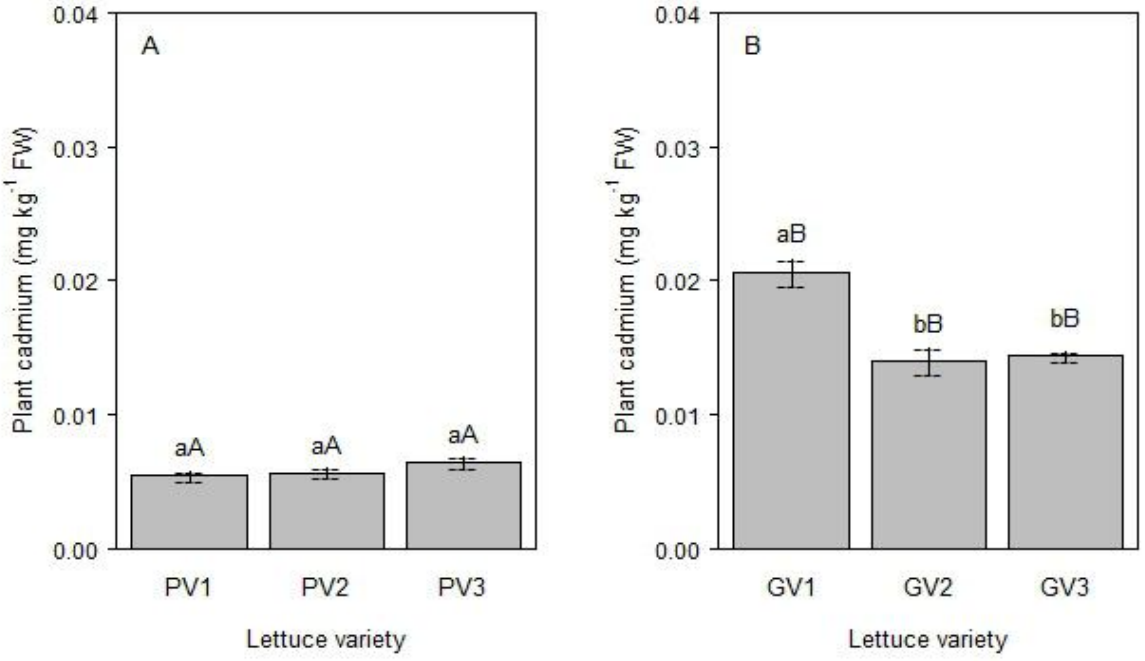

Figure E2 Cadmium (Cd) concentration in three iceberg lettuce varieties (mg kg-^{1} [FW]) from (A) Pukekohe (P) and (B) Gisborne (G). Mean (n = 4) and standard error indicated by the same lower case letter are not significantly different (*P* < 0.05) within a given site (lower case letters) or between sites (capital letters). Check font style and size.

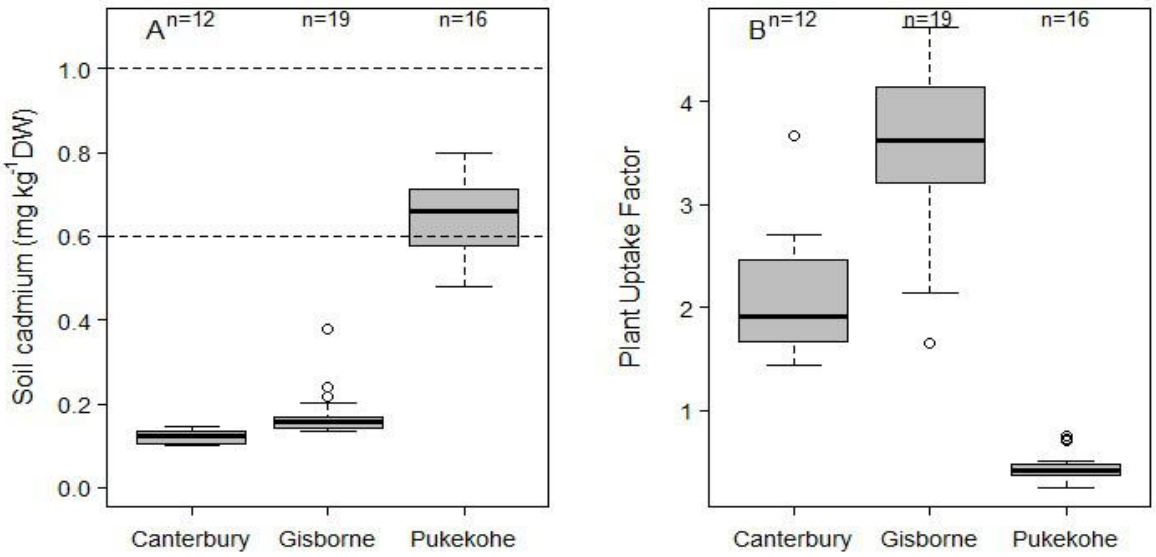

Figure E3. Regional variation in (A) soil Cd concentration and (B) plant uptake factor (PUF) for all lettuce types. The box extends from the 25th to 75th percentiles, with the median shown as a line in the box and whiskers showing upper and lower 1.5 times the interquartile range. The dashed horizontal lines in (A) show trigger values for the Tiered Fertiliser Management System tiers 1 and 2.

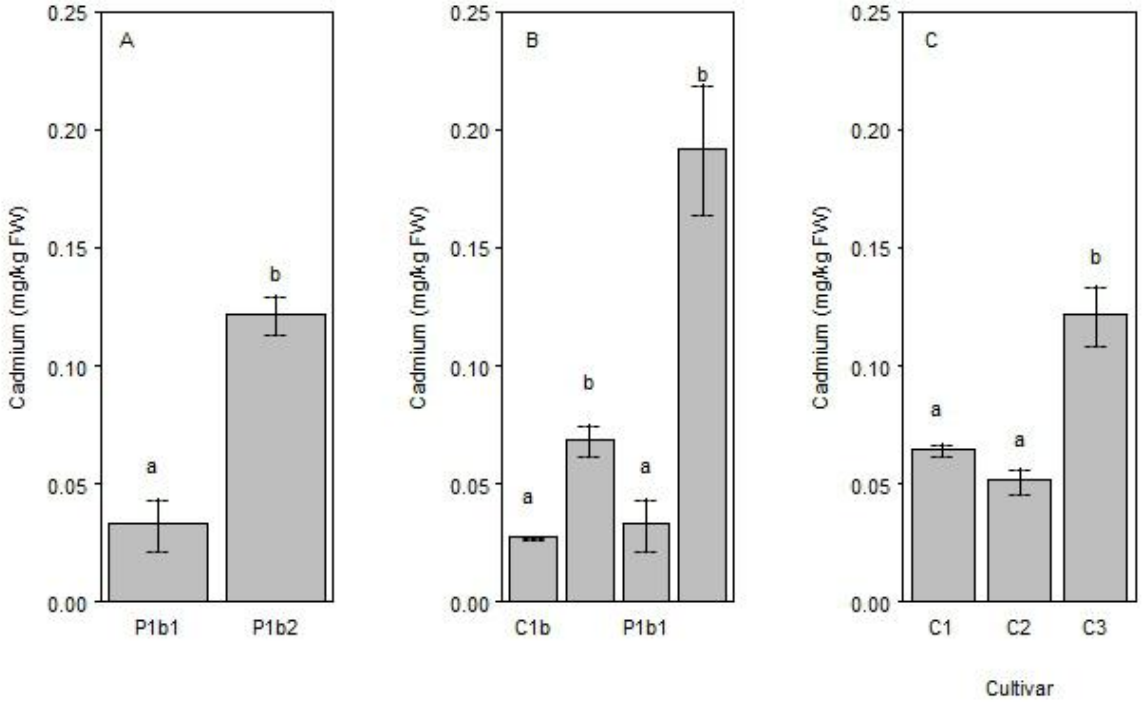

Figure E4. Cadmium concentration (mg kg^{-1} [FW]) in (A) two baby spinach crops harvested at different times at the same site (P1); (B) in baby and bunching spinach harvested from two sites. C = Canterbury, P = Pukekohe, b = baby, bu = bunching; and (C) three cultivars of bunching spinach grown at the same site but collected at different times. Mean (n = 3) and standard error indicated by the same lower case letter are not significantly different (*P* < 0.05) within a given site.

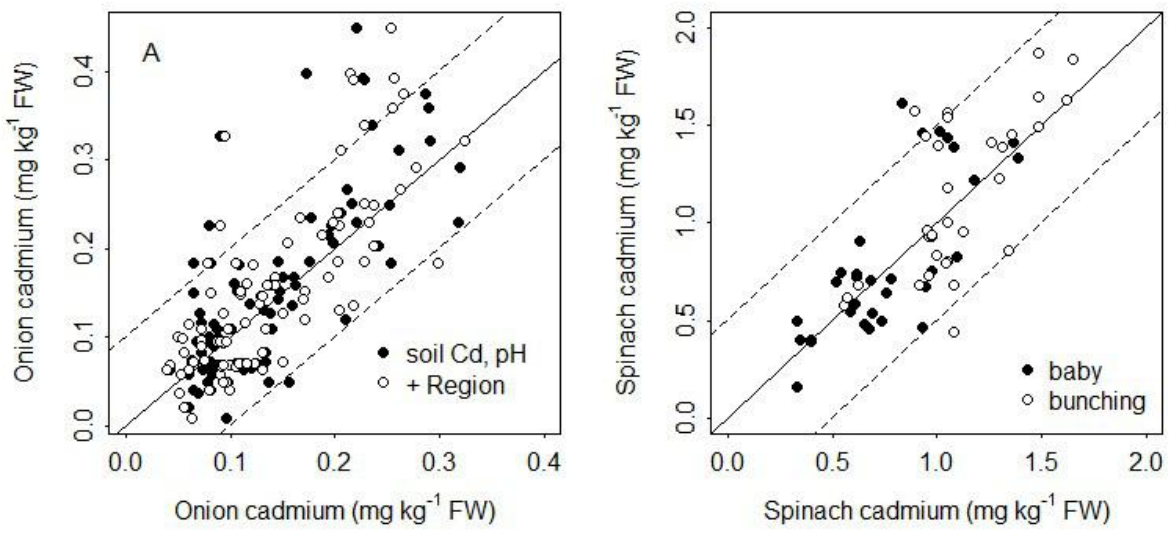

Figure E5. Relationship between predicted and actual (A) onion Cd concentrations (mg kg^{-1} [DW]) using equations 3 (open circles) and 4 (black circles) and (B) baby and bunching spinach. The solid line indicates the 1:1 fit.

Appendix F

Supplementary information in Chapter 7

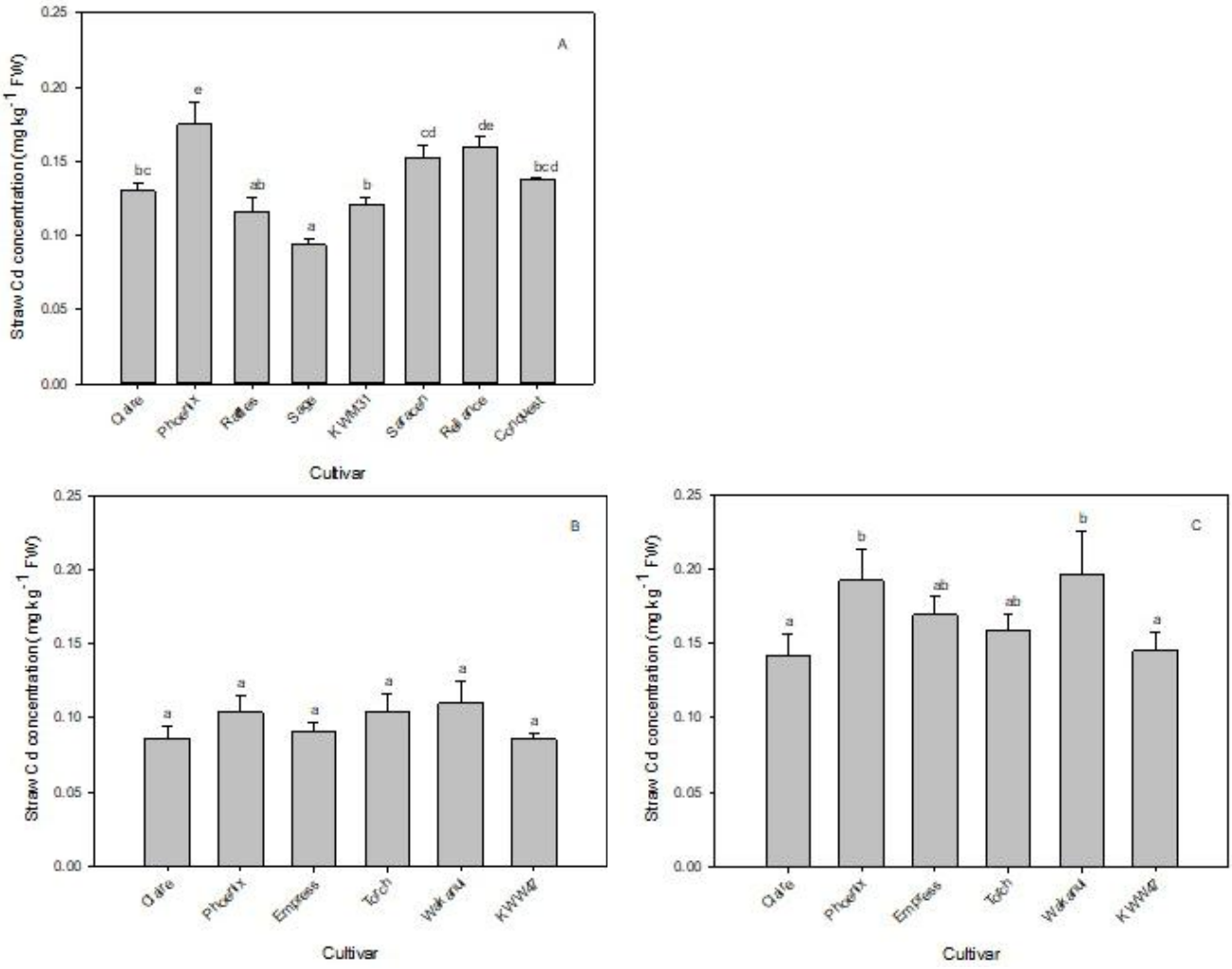

Figure F1 Mean wheat straw Cd concentrations (mg kg^{-1} FW) in different cultivars at A) Methven B) Temuka and C) Oreti site. Mean (n = 4) and standard error followed by the same letter are not significantly different (P < 0.05).

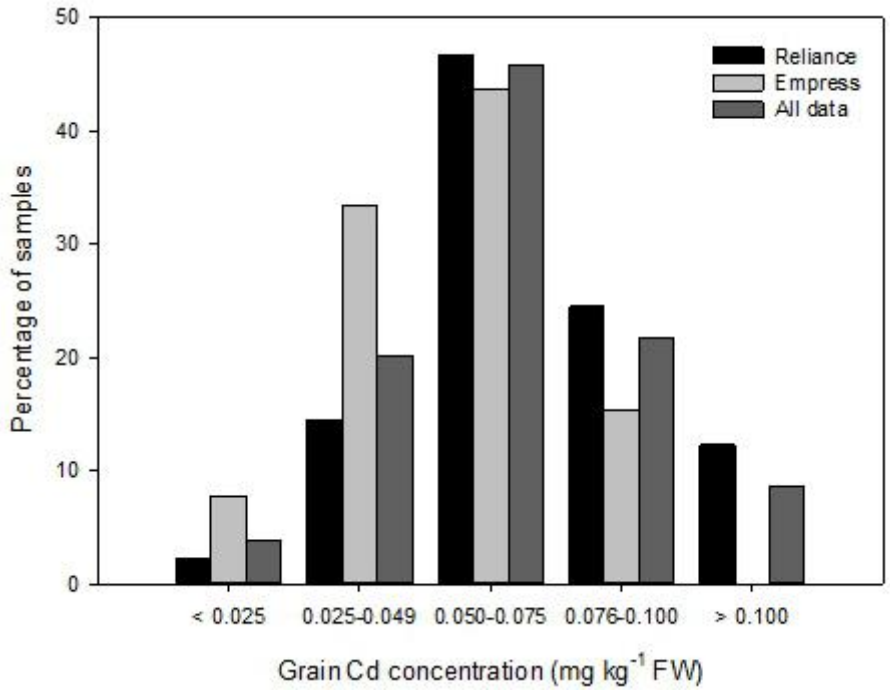

Figure F2. Frequency distribution of wheat grain Cd concentrations (mg kg^{-1} FW).